918. *A Spectroscopic Study of Some Pyrazine–Nickel*(II) *Complexes.*

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The visible and near-infrared spectra of a series of octahedral nickel(II) complexes containing pyrazine ligands are reported and the observed absorption bands assigned. Values for $10Dq$, the crystal-field splitting energy, and B, the Racah parameter, are deduced and interpreted. A reduction in the parameter $10Dq$ and an increase in the parameter B, in certain of the complexes, are attributed to steric repulsion. These observations are consistent with the postulate that the nickel–nitrogen bond is longer and is more ionic in these sterically hindered complexes. π-Bonding is believed to occur from the nickel atom to the pyrazine groups, becoming more important as the electronegativity of the attached halogen ligands decreases. Such behaviour is analogous to that postulated for substituted metal carbonyls. The visible absorption spectra of some diamagnetic square-planar complexes are discussed.

WE have reported earlier the chemistry of complexes formed by a number of transition metals with pyrazine and with its methyl-substituted derivatives, and have drawn conclusions, from spectral and magnetic data, about the structure of the complexes.[1-3] We discuss here the visible and near-infrared absorption of the nickel(II) derivatives. The data will be interpreted in terms of the theory outlined by Tanabe and Sugano,[4] and more recently by Liehr and Ballhausen,[5] Ballhausen,[6] and Jørgensen.[7]

In a cubic field, the ^3F ground state of the nickel(II) ion is split into three levels, the orbital single $^3A_2$ and the orbital triplets $^3T_1$ and $^3T_2$. With an octahedral arrangement of the ligands, the order of energies is $^3A_{2g} < {}^3T_{2g} < {}^3T_{1g}$ (Ia), whilst the reverse (Ib) is the case for a tetrahedral arrangement. The first excited term of the free nickel(II) ion, ^3P, transforms as $^3T_{1g}$ under cubic symmetry. There are therefore three spin-allowed transitions which may be observed in an octahedral complex, namely, ν_1 ($^3T_{2g} \longleftarrow {}^3A_{2g}$), ν_2 [$^3T_{1g}(F) \longleftarrow {}^3A_{2g}$], and ν_3 [$^3T_{1g}(P) \longleftarrow {}^3A_{2g}$]. The energies of these transitions[7] are readily expressed as functions of $10Dq$ and B. This energy scheme is very approximate, in the sense that configurational interaction between the various $^3T_{1g}$ states has not been allowed for. With this perturbation, the levels will therefore

[1] Lever, Lewis, and Nyholm, *Nature*, 1961, **189**, 58; in " Advances in the Chemistry of Coordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 419; *J.*, 1963, 3156.
[2] Lever, Lewis, and Nyholm, *J.*, 1962, 1235.
[3] Lever, Lewis, and Nyholm, *J.*, 1963, 5042.
[4] Tanabe and Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753, 766.
[5] Liehr and Ballhausen, *Ann. Physique*, 1959, **6**, 134.
[6] Ballhausen, " Introduction to Ligand Field Theory," McGraw-Hill, New York, 1962.
[7] Jørgensen, " Absorption Spectra and Chemical Bonding," Pergamon, London, 1962.

tend to move apart in energy. This interaction is taken into account in the calculations we have made, but we have, however, ignored spin–orbit coupling. B is related to the energy difference between spectroscopic terms. For terms of maximum multiplicity, the energy difference is dependent upon B alone. In the case of nickel(II), $E(^3F - {}^3P) = 15B$. The value of B found in complexes is always lower than that found in the free gaseous ion. This fact will be discussed below.

The intensities of the three spin-allowed transitions will be relatively low, since being d–d transitions, they are Laporte forbidden. In principle, four triplet–singlet transitions may also be observed in the spectral region generally studied (5000—30,000 cm.$^{-1}$). These are to the states ^1E_g ($t_{2g}^6 e_g^2$, ^1D), $^1A_{1g}$ ($t_{2g}^6 e_g^2$, ^1G), $^1T_{1g}$ ($t_{2g}^5 e_g^3$, ^1G), and $^1T_{2g}$ ($t_{2g}^5 e_g^3$, ^1D). Since these transitions are spin forbidden (as well as Laporte forbidden), they are expected to be particularly weak. Only the first transition should be observed in our case, since the other three lie in the ultraviolet region where they will be masked by other types of absorption bands.

In Table 1 are listed the diffuse-reflectance spectra of three classes of pyrazine–nickel complexes. In the first two groups the metal atom is paramagnetic and octahedral, whilst in the third group the complexes are diamagnetic and square-planar. These have already been discussed.[3] Although the complexes do not belong to the symmetry group

TABLE 1.

Diffuse-reflectance spectra (cm.$^{-1}$) of pyrazine–nickel complexes.

Group I (Octahedral complexes)				Group 2 (Octahedral complexes)			
$Pyz_2Ni(NCS)_2$	16,650		10,400	$MpNiCl_2$	23,000sh	13,150	12,500sh;
Pyz_2NiCl_2	16,150	12,200	10,500				11,500sh
$PyzNiBr_2$	15,750		10,400	$MpNiBr_2$	23,000sh	13,400b	
Pyz_2NiI_2	15,600		10,600	Mp_2NiI_2	*	13,600sh	13,000
$Mp_2Ni(NCS)_2$	16,000	12,800sh	10,400	$2,6$-Dmp_2NiCl_2	23,800	13,500b	12,100sh
$Mp_5Ni(NCS)_2$	16,650	12,600sh	10,500	$2,6$-Dmp_2NiBr_2	23,200sh	13,500b	
Mp_5NiCl_2	15,750	12,100sh	10,750;	$2,5$-$DmpNiCl_2$...	22,750	13,000	11,750
			ca. 10,000	Square-planar complexes			
Mp_5NiBr_2	15,800	12,200sh	10,300;	$2,5$-$DmpNiBr_2$	26,000	17,100	11,650w
			ca. 10,000	$2,5$-$DmpNiI_2$ ...	22,200	15,600	
Mp_5NiI_2...............	15,800	12,500sh	11,400	$2,6$-$DmpNiI_2$ ...	23,400	15,500b	11,400w
$2,6$-$Dmp_4Ni(NCS)_2$	16,650		10,400	Tmp_2NiI_2	24,400	15,200	
$2,6$-$Dmp_2Ni(NCS)_2$	16,150		10,400				

Pyz = Pyrazine.   Mp = Methylpyrazine.   Dmp = Dimethylpyrazine.   Tmp = Tetramethyl-pyrazine.

* Obscured by charge-transfer band.

O_h (most of them probably belong to D_{4h} or to groups of lower symmetry), there appears to be no definite splitting of the absorption bands which might have been expected to arise from such lower symmetry. There is, however, evidence for this in the broadness

TABLE 2.

Absorption spectra in methylpyrazine [ν (in cm.$^{-1}$) (ε)].

$Mp_5Ni(NCS)_2$	27,250 (287)	16,850 (13)	12,800 (4·5)	10,500 (16)
Mp_5NiCl_2.................	26,650 (282)	15,620 (8)	12,340 (1·8)	9200 (5)
Mp_5NiBr_2	26,650 (254)	15,470 (8·7)	12,000 (3·9)	8600 (5·0)
Mp_5NiI_2	25,000 (5180)	15,400 (9·4)	11,310 (1·2)	8100 (7·8)
		14,450sh		

of some of the bands. We shall assume, for the purpose of assignment, that they do belong to the point-group O_h.

Group 1.—The complexes are weakly coloured, with bands having low intensities in the visible region. Where measurements in solution have been made,[3] the extinction coefficients have been found to be of the order of 5—20 [see also $Mp_5Ni(NCS)_2$ (Table 2)]. Two main absorption bands are observed, at *ca.* 10,000 and at 15,000—17,000 cm.$^{-1}$ (Fig. 1). In addition, a weak band is observed in some of the complexes near 12,000 cm.$^{-1}$.

The main bands are relatively broad but show little structure. It is suggested that the band at *ca.* 10,000 cm.$^{-1}$ be assigned to ν_1 ($^3T_{2g} \longleftarrow {}^3A_{2g}$) and that at 15,000—17,000 cm.$^{-1}$ to ν_2 ($^3T_{1g}(F) \longleftarrow {}^3A_{2g}$). Using these energies, we can solve in each case for the parameters $10Dq$ and B. The results are listed in Table 3. The position of ν_3 can be computed
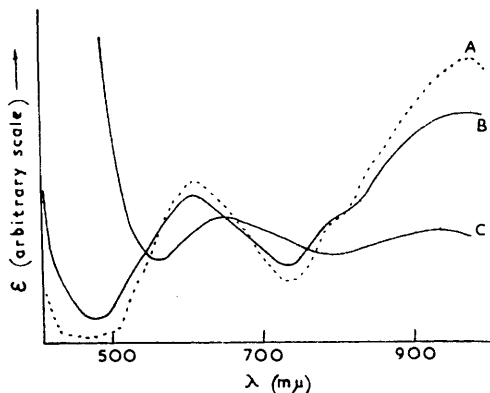

Fig. 1. Diffuse-reflectance spectra.
A, 2,6-Dmp$_4$Ni(NCS)$_2$. B, Pyz$_2$Ni(NCS)$_2$.
C, Pyz$_2$NiI$_2$.

and is found in all cases to lie in the ultraviolet region where it will be masked by ligand π–π* absorption and charge-transfer absorption. We may, however, consider an alternative assignment, namely, that the two main bands arise from the $^3T_{1g}(F) \longleftarrow {}^3A_{2g}$ (ν_2) and $^3T_{1g}(P) \longleftarrow {}^3A_{2g}$ (ν_3) transitions. This assignment, however, requires values of $10Dq$ and B which are too low to be acceptable. (The calculation shows that $10Dq$ would

TABLE 3.

Complex	$10Dq$ (cm.$^{-1}$)	β (cm.$^{-1}$)	β_1	β_2
Pyz$_2$Ni(NCS)$_2$ *	10,400	830	0·81	
Pyz$_2$NiCl$_2$ *.......................	10,500	650	0·63	0·68
Pyz$_2$NiBr$_2$ *	10,400	605	0·59	
Pyz$_2$NiI$_2$ *	10,600	540	0·52	
Mp$_5$Ni(NCS)$_2$	10,500	793	0·77	0·7
Mp$_5$NiCl$_2$...........................	10,000	724	0·70	0·67
Mp$_5$NiBr$_2$	10,000	738	0·72	0·68
Mp$_5$NiI$_2$	11,400	435	0·42	0·7
Mp$_2$Ni(NCS)$_2$ *	10,400	657	0·64	0·71
2,6-Dmp$_4$Ni(NCS)$_2$	10,400	830	0·81	
2,6-Dmp$_2$Ni(NCS)$_2$ *	10,400	694	0·67	
MpNiCl$_2$ *†	7940	825	0·80	0·68 ‡
MpNiBr$_2$ *†	8100	810	0·79	
2,6-Dmp$_2$NiCl$_2$ *	8200	804	0·78	0·67 ‡
2,6-Dmp$_2$NiBr$_2$ *	8100	825	0·80	
2,5-Dmp·NiCl$_2$ *†	7860	811	0·79	0·65 ‡
[Tetrahedral Species in Solution]				
Mp$_5$NiCl$_2$...........................	5000	810	0·79	0·78
Mp$_5$NiBr$_2$	4650	820	0·80	0·76
Mp$_5$NiI$_2$	4350	825	0·80	0·71

$\beta_1 = B/B_0$ ($B_0 = 1030$ cm.$^{-1}$); β_2, see text.
* Bridging halogen. † Bridging pyrazine. ‡ Assuming assignment of the singlet state.

be in the range 6000—6500 cm.$^{-1}$ and B in the range 400—500 cm.$^{-1}$.) It seems unlikely that an octahedral nickel complex containing nitrogen ligands could have such a low crystal-field splitting energy. Moreover, certain of the complexes have been examined in the range 6,000—7,000 cm.$^{-1}$, where a ν_1 band should appear if the above assignment is correct, and no bands were observed. We conclude that the two bands are ν_1 and ν_2, and that the weak band near 12,000 cm.$^{-1}$ probably arises from the transition ^1E_g (^1D) $\longleftarrow {}^3A_{2g}$.

Group 2.—In the second class of octahedral complexes, a broad band with some structure is observed in the region 11,750—13,600 cm.$^{-1}$ and a sharper band is observed near

23,000 cm.$^{-1}$ (Fig. 2). This latter band is sometimes seen as a shoulder on the tail of the charge-transfer absorption (see below).

These two main bands are assigned as ν_2 and ν_3, respectively. Table 3 lists the values of $10Dq$ and B calculated on this basis (the high-energy maximum of ν_2 was used in this calculation). The structure on the lower-energy band may be due to spin–orbit coupling, asymmetry of the ligand field, or to the $^1E_g \longleftarrow {}^3A_{2g}$ transition which may borrow intensity from the neighbouring triplet band. The nature of a band structure of this type in nickel(II) complexes has been discussed by Ballhausen [6] and by Jørgensen.[8]

The alternative assignment of the red band as ν_1 and the blue band as ν_2 may be eliminated on the grounds that it would imply a value for B which is some three times larger than that observed in the free ion, and such high values of B have never been observed.

Group 3.—An X-ray determination of dibromo-(2,5-dimethylpyrazine)nickel(II) has shown [3,9] that this diamagnetic complex is polymeric, involving four-co-ordinate square-planar Ni(II), with bridging occurring through the pyrazine units. The steric hindrance
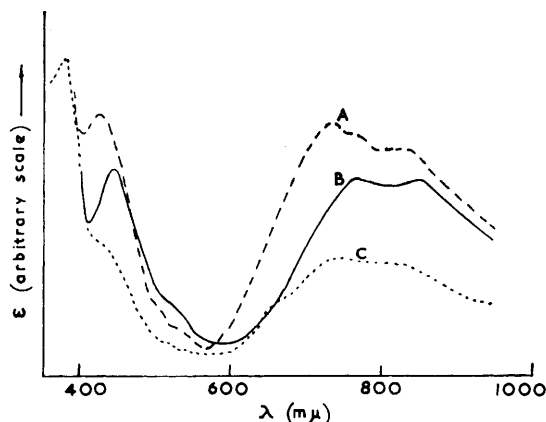

FIG. 2. Diffuse-reflectance spectra.
A, 2,6-Dmp$_2$NiCl$_2$. B, 2,5-DmpNiCl$_2$.
C, MpNiCl$_2$.

between the methyl groups and the bromine atoms is reduced by the rotation of the pyrazine unit through 90°. It may be regarded as a *trans* square-planar complex in which the pyrazine units have been rotated from the xy plane into the xz plane.[3] Assuming π bonding between the pyrazine ring and the d_{xy} orbital, the single electron energies are most likely in the sequence:

$$d_{xy} < d_{z^2} < d_{xz} = d_{yz} < d_{x^2-y^2}$$

However, there is some uncertainty as to the relative order of the d_{xy} and the d_{xz}, d_{yz} pair of orbitals. We assume that the other diamagnetic complexes are analogous. The spectra of square-planar complexes of nickel are not as well understood as are those of the tetrahedral or octahedral complexes. Recently, a full molecular-orbital treatment of diamagnetic nickel complex has been made by Gray and Ballhausen.[10] Their scheme, though not directly applicable to the spectra of these complexes, may be used as a guide to the assignments. The main band near 600 mμ (Fig. 3) is assigned as arising from the transition $d_{x^2-y^2} \longleftarrow d_{xy, yz}$. The stronger absorption near 400 mμ is probably a charge-transfer band from a d orbital on the metal to an antibonding π orbital located mainly on the ligand. The weak absorption near 800 mμ, seen in some of the complexes, is probably a spin-forbidden transition to a triplet state.

We find that the crystal-field strength of pyrazine is comparable with that of pyridine. However, the complexes formed by α-substituted pyrazines with nickel differ markedly from those formed by α-substituted pyridines. Thus the pyridine complexes appear to be

[8] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.
[9] Ayres, Robertson, and Pauling, *Inorg. Chem.*, 1964, **3**, 1303.
[10] Gray and Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

tetrahedral whilst the pyrazine complexes are planar. It has been suggested that steric repulsion in methyl-substituted pyridine–nickel complexes is reduced by the formation of tetrahedral molecules.[11] The formation of square-planar pyrazine complexes may be attributed either to a favourable lattice energy or to electronic effects. Di-iodobispyridine-nickel(II) is tetrahedral,[11] whilst di-iodobisquinolinenickel(II) is square-planar.[12] If the only contributing factors were steric ones, then one would have expected that the bulky quinoline ligand would have preferred a stereochemistry offering the minimum steric interaction between adjacent ligands, namely, a tetrahedral arrangement. Quinoline should, however, be a better π-electron acceptor than pyridine. It seems possible that, in

Fig. 3. Diffuse-reflectance spectra.
A, Imp_2NiI_2. B, $2,6\text{-}DmpNiI_2$. C, $2,5\text{-}DmpNiBr_2$.
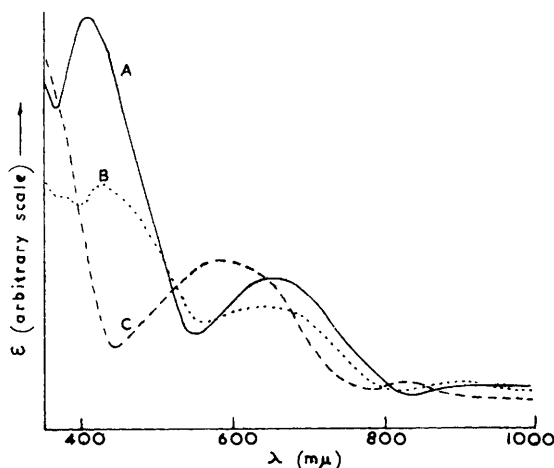
order to make the best use of the increased back-donation, the nickel ions prefer a square-planar environment. The formation of square-planar pyrazine complexes may therefore be attributable to the presence of strong π-bonds from nickel to pyrazine.

Solution Spectra in Methylpyrazine.—All pyrazine–nickel complexes, whether in the solid state or in solution, exhibit a relatively strong band [3] (ε 50—300) in the region 25,000—27,000 cm.$^{-1}$. Such a band is absent from the spectra of the free ligands, and is almost certainly a charge-transfer band. As the pyrazine ligand is readily reducible, the transition is probably $\pi^* \longleftarrow d_\gamma$.

The spectrum of $Mp_5Ni(NCS)_2$ in methylpyrazine is virtually identical with the diffuse-reflectance spectrum of the solid (Tables 1 and 2). The species in solution is evidently the octahedral $Mp_4Ni(NCS)_2$. (The infrared spectrum of the solid indicates that both NCS groups are covalently bound.[3]) On the other hand, the three complexes Mp_5NiX_2 (X = Cl, Br, or I) have spectra in methylpyrazine which differ from their diffuse-reflectance spectra (see Fig. 4). The reflectance spectrum, however, is limited to measurements below 1000 mμ. Within the range 500—1000 mμ, it is possible to assign the spectra to an octahedral [3] arrangement, providing that there is no band above 1000 Å. It is possible that the low-frequency band observed for the solution is present in the solid; if this is so, it is not possible to assign the stereochemistry to an octahedral arrangement.

On the assumption that the near-infrared band in solution is ν_1, then B must be con-considerably in excess of the free-ion value for ν_2 to have the observed energy. If the near-infrared band is taken to be ν_2, then the value of $10Dq$ is too low to be acceptable ($10Dq = 5700$, 5250, and 4800 cm.$^{-1}$ and $B = 500$, 560, and 600 cm.$^{-1}$ for the chloride, bromide, and iodide, respectively). The values of B required, although not too low, lie in the reverse sequence from that which would be expected.

[11] Glonek, Curran, and Quagliano, *J. Amer. Chem. Soc.*, 1962, **84**, 2014.
[12] Goodgame and Goodgame, *J.*, 1963, 207.

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The corresponding cobalt(II) complexes dissolve in methylpyrazine to give tetrahedral species.[2] If we assume that the nickel complexes are also tetrahedral in solution, we find that the observed frequencies can be fitted very readily into the secular equation for nickel in a tetrahedral field.[7] The band in the near-infrared region would then be assigned as ν_2 ($^3A_2 \longleftarrow {}^3T_1$) and that in the visible region as ν_3 [$^3T_1(P) \longleftarrow {}^3T_1$] (see I*b*). Weak absorption observed in the region expected for the two triplet–singlet transitions could be due to transition to the ^1D state (Table 3). The values of $10Dq$ and B obtained are similar
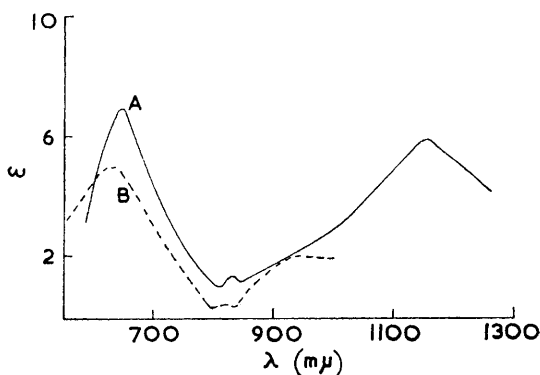

Fig. 4. Spectra of Mp_5NiBr_2.
A, In solution in methylpyrazine.
B, Diffuse-reflectance spectrum (arbitrary scale for ε.

to the values obtained from the spectra of those pyrazine–cobalt complexes which are undoubtedly tetrahedral.[2,13] However, this must only be regarded as a tentative assignment, since the intensity of the ν_3 absorption is much lower than that generally associated with tetrahedral nickel derivatives.[14]

DISCUSSION

In those cases where ν_1 ($=10Dq$) in octahedral complexes was observed, the value of B was obtained by putting the energy (in wavenumbers) of ν_2 into the secular equation. Where ν_2 and ν_3 only were observed, the secular equation was solved by trial and error, aided by the fact that $E(\nu_2) \approx 17 \cdot 5\ Dq$. The results in the latter case were checked by means of the " diagonal sum rule," $\nu_2 + \nu_3 - 30Dq = 15B$. Since the parameters $10Dq$ and B are solutions of the secular equation, their accuracy is only limited by that with which the positions of the absorption bands can be determined. B is probably accurate to within ± 50 cm.$^{-1}$, and $10Dq$ to within ± 200 cm.$^{-1}$. The accuracy is, of course, also controlled by the limitations in theory.

We shall discuss only the trends in the data we have obtained, rather than the actual values. The two classes of octahedral complexes differ in their values of $10Dq$, the splitting being about 2000 cm.$^{-1}$ higher in the first class than in the second. The Racah parameter, B, has higher values in this latter group than the chlorides and bromides in the former group. This may be understood if we assume that in the first group the metal bonds to an unhindered nitrogen atom, whilst in the second group bonding is to a nitrogen atom hindered by a methyl group *ortho* to it.[2,3] Presumably in the latter case, the bond is slightly longer to minimise steric repulsion, thus decreasing $10Dq$, and, by making the bond more ionic, increasing B (see below). Drago *et al.*,[15] working with *N*-substituted amides, have shown that there is a reduction in $10Dq$ as steric effects become important, despite the increase in base strength of the donor atom.

[13] Lever, Lewis, and Nyholm, unpublished work.
[14] Gill and Nyholm, *J.*, 1959, 3997; Cotton, Faut, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.
[15] Drago, Meek, Joesten, and LaRoche, *Inorg. Chem.*, 1963, **2**, 124.

In the spectrochemical series, the crystal-field strengths of the anions decrease in the order $NCS^- > Cl^- > Br^- > I^-$. We would expect, and generally do find, that where the anion forms part of a complex, the mean crystal-field strength of that complex would follow the same order. We note, however, that in the pyrazine series of complexes, the mean crystal-field strength of the complexes remains essentially constant. A similar, though not quite so pronounced, situation exists in the octahedral methylpyrazine series. It is reasonable to assume that the contribution to the mean crystal-field strength by the halogens does decrease in the sequence expected, so that we must conclude that there is some mechanism which compensates for this decrease. The crystal-field splitting energy in the purely electrostatic model is the difference in energy between the t_{2g} (or d_ϵ) and e_g (or d_γ) orbitals. However, in ligand-field theory, the metal d orbitals are allowed to interact with σ and π orbitals on the ligand. In this theory, the e_g orbitals have antibonding character, whilst the t_{2g} orbitals, having π symmetry with respect to the ligands, may have π-bonding or antibonding character. If the ligands are capable of accepting π electrons from the metal, then the crystal-field splitting may be increased by the reduction in energy of the t_{2g} orbitals.

The pyrazine unit, being readily attacked by nucleophiles,[16] should be capable of accepting electrons from the metal into its antibonding π orbitals. The degree of π bonding which is present will depend not only on the acceptor strength of the ligand but also upon the π-donor ability of the nickel ion. The ease with which nickel will donate d electrons will depend upon its effective electronegativity in the complex; this will, in turn, depend upon the nature of the other groups attached to it. As the electronegativity of the attached halogen decreases, we may expect more charge to be moved on to the metal. The ability of the metal to donate electrons should, therefore, increase in the order $NCS^- < Cl^- < Br^- < I^-$. This is, of course, similar to the situation existing in substituted metal carbonyls. Hence we understand that the crystal-field splitting will be compensated for the reduction in the crystal-field strength of the halogen, by an increase in π bonding with the pyrazine ligand.

It is well known that the value of the Racah parameter, B, is always lower in a complex than in the free gaseous ion.[17,18] This parameter relates to the mutual repulsion between electrons (interelectronic repulsion) in the valency shell. It may be reduced by three mechanisms. In the first, " central field covalency," [19] the presence of σ electrons from the ligands reduces the effective charge felt by the d electrons, hence allowing the d shell to expand. The interelectronic repulsion would accordingly be reduced. In the second, " symmetry restricted covalency," [20] d electrons from the metal are delocalised into σ-antibonding, or into π-bonding or π-antibonding, orbitals, thus spending part of their time on the ligand. This delocalisation leads to a reduction in interelectronic repulsion. The third mechanism involves the first-order perturbation of the ligand field on excited terms of the electron configuration, *i.e.*, the mixing in of $d^{n-1}s$ and $d^{n-1}p$ into the d^n ground state. Both Schlafer [21] and Moffitt and Ballhausen [22] have discussed this last mechanism.

Unfortunately, it is not easy to distinguish between a reduction in B arising from " central field covalency " and one arising from " symmetry restricted covalency." The relatively high values of B observed in the second group of octahedral complexes can be readily understood to result from the high degree of ionic bonding present in the longer bonds.

The increase in the π bonding to the pyrazines in the first group should show itself in a rapid decrease in B (or in $\beta_1 = B/B_0$, where B_0 is the value of B in the free gaseous ion),

[16] Krems and Spoerri, *Chem. Rev.*, 1947, **40**, 279.
[17] Dunn, *J.*, 1959, 623.
[18] Jørgensen, *Adv. Chem. Phys.*, 1963, **5**, 33.
[19] Orgel, *J. Chem. Phys.*, 1955, **23**, 1819, 1824, 1958.
[20] Van Vleck, *J. Chem. Phys.*, 1935, **3**, 803, 807.
[21] Schlafer, *Z. phys. Chem. (Frankfurt)*, 1956, **6**, 201.
[22] Moffitt and Ballhausen, *Ann. Rev. Phys. Chem.*, 1956, **7**, 103.

being a reduction arising from " symmetry restricted covalency." This reduction in B is observed. However, we may also expect a reduction due to " central field covalency," because of the increasing polarisability of the halogens ($NCS^- < Cl^- < Br^- < I^-$). These two phenomena would therefore supplement one another.

We have been unable to observe any variation in crystal-field strength as a function of methyl-group substitution, and assume that it is too small to be detected. Increasing the number of methyl substituents would tend to increase the crystal-field strength through stronger bonding, since the substituted ligands are, of course, stronger bases.[23] However, the methyl substituents would increase the charge density in the ring, making it a poorer π acceptor, and hence reducing the crystal-field strength. These two effects may tend to cancel one another. The ^1E_g state arises from the configuration $t_{2g}^6 e_g^2$, and its energy[7] relative to $^3A_{2g}$ is approximately given by $8B + 2C$. The ratio β_2 (Table 3) relates the energy of this state in the complex to its energy in the free gaseous ion ($B = 1030$ cm.$^{-1}$, $C/B = 4709$; hence $8B + 2C = 17{,}940$ cm.$^{-1}$). The ratio β_2 is found to be comparable with β_1. A similar observation was made by Bostrup and Jørgensen[24] in their study of the β_1 and β_2 ratios of a range of nickel(II) derivatives.

We have also sought to distinguish between bridging and terminal pyrazine units[1] by means of their crystal-field strengths. Assuming a purely electrostatic bond and a symmetrical ligand, the crystal-field strength should be essentially independent of whether the ligand is terminal or bridging. However, if covalent bonds are formed, there will be differences, since two metal atoms will be competing for the same set of ligand molecular orbitals. We have been able to detect a difference in the cobalt series; the visible spectrum of the pale blue $PyzCoCl_2$, containing bridging pyrazine,[13] is shifted significantly to lower energies compared with the spectrum of the pink Pyz_2CoCl_2, containing terminal pyrazine groups.[2] In the nickel series, the crystal-field strength of the terminal pyrazine members of the second class of octahedral complexes is only marginally higher than that of the bridging members of the same group. We would not, however, expect there to be much of a difference here, in view of the high degree of ionic character present in these complexes. We have not yet been able to prepare any bridging pyrazine complexes in the first octahedral class. Finally, we note that the maximum crystal-field strength of pyrazine is greater than that of pyridine,[24] despite the fact that pyridine is a stronger base by a factor of *ca.* 10^4. Presumably, therefore, back-donation is considerably more important in pyrazine chemistry than in pyridine chemistry, as we have previously concluded.

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