stable (relative to tetrahedral CoL_2X_2) where L = 3-methylpyridine than when L = pyridine, 4-methylpyridine, or isoquinoline.[23] Second, values of $10Dq$ for mononuclear six-coordinate Ni(II) complexes, NiL_4X_2 (X = NCO, NCS, NCSe, and N_3), are consistently smaller for L = 3-methylpyridine than for other amines.[6] Detailed discussion of these results in terms of the charge distribution in the pyridine ring will be published elsewhere.

It is pertinent to ask whether the value of $10Dq$ is increased further in the iodo complexes. This information is not readily available since very often the "corresponding" iodo complex turns out to be square or tetrahedral, rather than octahedral.[3-5] Where octahedral complexes are obtained, charge-transfer absorption generally prevents ν_3 from being identified. As the electron density increases on the nickel ion we may anticipate that square complexes would be formed with good π-acceptor amines, while tetrahedral complexes may be anticipated with other amines.[12] This is in general observed.

The ligand with the highest crystal field strength in this study is acetonitrile, which though not an amine was included because it gives the same microsymmetry about the nickel ion. The high R value implies that it is a good π-acceptor.

There is evidence that steric effects may be important since in general it appears that sterically hindered amines have the lower crystal field strengths. This is illustrated by the fact that methylpyrazine, 2,5-dimethylpyrazine, and quinoxaline lie below 2,6-dimethylpyrazine in the spectrochemical series. Only in complexes of the last mentioned ligand are the coordinating nitrogen atoms unhindered.[4] Similarly, $10Dq$ for quinoline is the lowest for the pyridine series of complexes. Presumably, in order to minimize interligand repulsions, some or all of the bonds in these complexes are lengthened, thus reducing the mean value of $10Dq$. It is, of course, also possible that $10Dq'$ is smaller in these cases because the amine is acting as a bridging ligand.

The variation in the Racah parameter B, a measure of the interelectronic repulsion, is small. In nearly all the cases the bromo complex has the lower value. However, this may be due as much to central field covalency as to symmetry restricted covalency (back donation).[11]

Acknowledgment.—T. M. S. thanks the Ministry of Education of Northern Ireland for a Research Studentship and the Queen's University of Belfast for a Foundation Scholarship.

[23] H. C. A. King, E. Körös, S. M. Nelson, and T. M. Shepherd, Abstracts, Eighth International Conference on Coordination Chemistry, Vienna, 1964, p. 338, and unpublished work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE QUEEN'S UNIVERSITY, BELFAST, NORTHERN IRELAND

Metal-to-Ligand π-Bonding in Some Nickel(II) Pseudo-Halide Complexes with Heterocyclic Aromatic Amines

BY S. M. NELSON AND T. M. SHEPHERD

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The electronic spectra and magnetic moments for a series of complexes NiL_4X_2 are reported (L = pyridine, 3-methylpyridine, 4-methylpyridine, or isoquinoline; X = NCO, NCS, NCSe, or N_3). An analysis of the spectra indicates that deviations from O_h symmetry are small in all cases. Derived ligand field parameters, $10Dq$ and B, lead to the following orders for the anionic ligands in the spectrochemical and nephelauxetic series, respectively, NCSe > NCS > NCO > N_3 and NCO > NCS > NCSe > N_3. A smaller but significant variation in $10Dq$ is observed with change of neutral ligand. Here the order is isoquinoline > pyridine $\sim$ 4-methylpyridine > 3-methylpyridine. The observed ligand field strengths of both series of ligands are discussed in terms of metal–ligand π-bonding and an explanation for the apparently greater π-acceptor capacity of pyridine and 4-methylpyridine compared with 3-methylpyridine is proposed. A number of complexes of stoichiometry NiL_2X_2 (X = NCS, NCSe, and N_3, but not NCO) are also reported. These have six-coordinate polymeric structures comprising bridging pseudo-halide ions.

Although it is generally accepted that highly conjugated amines such as 1,10-phenanthroline and 2,2′-dipyridyl can act as moderately good π-acceptors when complexed with transition metals ions,[1] the evidence for π-orbital overlap in metal–pyridine bonds is much less, at least for M^{2+} ions of the first transition series.[2] However, recent work[3,4] in this laboratory on the thermodynamics of tetrahedral–octahedral equilibria in solutions of mixed complexes of cobalt(II) halides and pseudo-halides with pyridine derivatives suggested that such d_π–p_π bonding can be important here also and, further, that its extent is governed by the nature of the anionic ligand partner. Evidence was also presented for a measure of metal→X

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[1] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

[2] C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, 1963, p. 71.

[3] H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

[4] H. C. A. King, E. Körös, and S. M. Nelson, *ibid.*, 4832 (1964).

(X = pseudo-halide) π-bonding, the relative abilities of X for accepting back-coordinated electrons being NCSe > NCS > NCO. Since the extent of d-orbital splitting in transition metal complexes is believed to be sensitive to metal–ligand π-bonding it might be expected that variations in the π-acceptor properties of both the aromatic amines and the pseudo-halide ions would be reflected in the ligand field parameters. In order to examine the effect of the pseudo-halides and the aromatic amines in mixed complexes of the same type used in the thermodynamic work we have obtained the electronic spectra of a series of NiL_4X_2 complexes, where L = pyridine, 3-methylpyridine, 4-methylpyridine, or isoquinoline and X = NCO, NCS, NCSe, or N_3. Six-coordinate Ni(II) complexes rather than Co(II) complexes were chosen for study because the better separation of the d–d bands renders them more amenable to detailed analysis.

Experimental

Preparation of NiL_4X_2 Complexes.—The preparation of the thiocyanates was as described previously.[5] For the cyanates and azides an aqueous solution of hydrated nickel nitrate (1 mole) was mixed with a freshly prepared cold aqueous solution of sodium cyanate or potassium azide (2 moles) to which an aqueous ethanolic solution of the appropriate amine (~4.5 moles) was added with vigorous stirring. Blue or blue-violet crystals of the products separated on standing. They were recrystallized from chloroform containing added amine, washed with a small amount of cold carbon tetrachloride, dried in air, and stored in a desiccator.

The selenocyanates were prepared similarly except that the amine was added to the nickel nitrate solution before the potassium selenocyanate. This was to ensure an alkaline environment for the selenocyanate at all times, thereby avoiding precipitation of selenium.

NiL_2X_2 Complexes.—The azides were readily formed by allowing the finely divided parent tetrakisamine complexes to stand in warm air for 1–2 days, or by warming to 40–50° in chloroform, followed by filtration.

The thiocyanates were prepared by heating the tetrakisamine complexes in an oven at ~100°, or by refluxing in benzene for several hours followed by filtration while still hot and washing with hot benzene.

Diselenocyanatobis(pyridine)nickel(II) was the only selenocyanate of this stoichiometry prepared. The preparation was similar to that of the tetrakis pyridine complex except that only 1.8-mole proportions of potassium selenocyanate were used, the precipitation was carried out at 80°, and the reaction mixture was maintained at that temperature for 30 min. The green product was washed with hot water, ethanol, and finally a small amount of carbon disulfide to remove any elemental selenium that may have formed.

All the complexes were analyzed for nickel by EDTA titration in ammonia–ammonium chloride buffer at 35° using murexide indicator. Prior to titration the selenocyanato complexes were decomposed by gently boiling in a pH 10 buffer solution. The other compounds were dissolved initially in dilute hydrochloric acid. The analytical data are given in Table I, along with the magnetic moments corrected for diamagnetism. No analytical data are included for the tetrakisamine azides. These blue complexes lost amine rapidly on standing to form green compounds of stoichiometry $NiL_2(N_3)_2$. All analyses indicated that considerable loss of amine had occurred by the time the crystals were isolated in a dry state. The bisamine complexes are stable at least to 100° but at temperatures much in excess of this they explode violently.

TABLE I

ANALYTICAL DATA AND MAGNETIC MOMENTS OF NICKEL(II) COMPLEXES

Complex	Nickel, % Found	Nickel, % Calcd.	Magnetic moment μ_{eff}, B.M.	Temp., °C
$Ni(py)_4(NCO)_2$[a]	12.75	12.78	3.17	16.0
$Ni(\beta\text{-pic})_4(NCO)_2$[a]	11.40	11.39	3.10	16.0
$Ni(\gamma\text{-pic})_4(NCO)_2$[a]	11.37	11.39	3.12	16.0
$Ni(IQ)_4(NCO)_2$[a]	9.03	8.93	3.06	18.4
$Ni(py)_4(NCS)_2$	11.98	11.95	3.13	15.0
$Ni(\beta\text{-pic})_4(NCS)_2$	10.81	10.70	3.13	18.4
$Ni(\gamma\text{-pic})_4(NCS)_2$	10.68	10.70	3.11	18.5
$Ni(IQ)_4(NCS)_2$	8.50	8.48	3.16	18.4
$Ni(py)_4(NCSe)_2$	10.07	10.05	3.20	17.0
$Ni(\beta\text{-pic})_4(NCSe)_2$	9.18	9.16	3.10	17.5
$Ni(\gamma\text{-pic})_4(NCSe)_2$	9.20	9.16	3.06	17.6
$Ni(py)_2(N_3)_2$	19.52	19.50	3.00	20.0
$Ni(\beta\text{-pic})_2(N_3)_2$	17.73	17.84	3.10	20.0
$Ni(\gamma\text{-pic})_2(N_3)_2$	17.76	17.84	3.24	20.0
$Ni(IQ)_2(N_3)_2$	14.80	14.70	3.09	18.4
$Ni(py)_2(NCS)_2$	17.70	17.63	3.26	19.0
$Ni(\beta\text{-pic})_2(NCS)_2$	16.25	16.27	3.28	16.7
$Ni(\gamma\text{-pic})_2(NCS)_2$	16.31	16.27	3.17	16.7
$Ni(IQ)_2(NCS)_2$	13.55	13.55	3.20	16.9
$Ni(py)_2(NCSe)_2$	13.80	13.75	3.28	19.0

[a] py = pyridine; β-pic = 3-methylpyridine; γ-pic = 4-methylpyridine; IQ = isoquinoline.

Physical Measurements.—The electronic spectral, magnetic, and thermogravimetric measurements were carried out as described previously.[3–5] Infrared spectra were recorded on a Perkin-Elmer Model 21 instrument in potassium bromide disks and in Nujol mulls.

Results

NiL_4X_2 Complexes.—The complex $Ni(py)_4(NCS)_2$ has been fairly fully investigated. From X-ray studies Porai-Kojics, *et al.*,[6] have shown that it has a *trans*-octahedral structure with Ni–N(pyridine) and Ni–N(thiocyanate) distances of 2.00 Å. The electronic reflectance spectrum has been reported by Bostrup and Jørgensen.[7] No splitting of any of the spectral bands was observed and tetragonal distortion was concluded to be small. The absence of tetragonal distortion in the related complex $Ni(NH_3)_4(NCS)_2$ has recently been demonstrated by Hare and Ballhausen from an analysis of the polarized crystal spectra.[8]

The room-temperature magnetic moments for all the tetrakisamine complexes except the azides, which were too unstable for accurate determination, are given in Table I. The values fall in the narrow range 3.06–3.20 B.M. and are consistent with an octahedral structure for the complexes. Table II lists the spectral bands both in the solid state (30,000–10,000 cm.$^{-1}$) and in chloroform or nitromethane solution (30,000–5000 cm.$^{-1}$). The addition of a small quantity of free amine to the solutions was necessary in order to suppress decomposition to insoluble products, usually NiL_2X_2. The ease of dissociation of the tetrakisamine complexes is N_3 > NCO > NCS > NCSe. No re-

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[5] S. M. Nelson and T. M. Shepherd, *J. Chem. Soc.*, in press.

[6] M. A. Porai-Kojics, A. S. Antzishkina, L. M. Dickareva, and E. J. Jukhov, *Acta Chem. Scand.*, **11**, 1223 (1957).

[7] O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

[8] C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF NiL_4X_2 COMPLEXES

Complex	State	Frequency, cm.$^{-1}$ [a]
$Ni(py)_4(N_3)_2$	Soln.[b]	25,840, 16,210 (16), 12,320 sh, 9,800 (25)
$Ni(\beta\text{-pic})_4(N_3)_2$	Soln.[b]	25,770, 16,080 (17), 12,350 sh, 9,790 (23)
$Ni(\gamma\text{-pic})_4(N_3)_2$	Soln.[b]	25,710, 16,230 (16), 12,380 sh, 9,800 (25)
$Ni(IQ)_4(N_3)_2$	Soln.[b]	16,310 (18), 12,330 sh, 9,870 (26)
$Ni(py)_4(NCO)_2$	Soln.[c]	26,810, 16,610 (10), $\sim$13,000 sh, 10,050 (11)
	Solid	26,880, 16,560
$Ni(\beta\text{-pic})_4(NCO)_2$	Soln.[c]	26,670, 16,560 (10), $\sim$13,000 sh, 10,010 (11)
	Solid	$\sim$26,800 (sh), 16,580, $\sim$13,000 sh
$Ni(\gamma\text{-pic})_4(NCO)_2$	Soln.[c]	26,670, 16,610 (17), $\sim$13,000 sh, 10,040 (10)
	Solid	$\sim$26,800 sh, 16,580, $\sim$13,000 sh
$Ni(IQ)_4(NCO)_2$	Soln.[c]	16,640 (9), $\sim$13,000 sh, 10,080 (11)
	Solid	16,600, $\sim$13,000 sh
$Ni(py)_4(NCS)_2$	Soln.[c]	$\sim$22,200 sh, 16,900 (23), $\sim$12,800 sh, 10,450 (27)
	Solid	16,950, $\sim$12,800 sh, 10,470
$Ni(\beta\text{-pic})_4(NCS)_2$	Soln.[c]	$\sim$22,500 sh, 16,900 (24), $\sim$12,800 sh, 10,400 (28)
	Solid	16,900, $\sim$12,700 sh, 10,400
$Ni(\gamma\text{-pic})_4(NCS)_2$	Soln.[c]	$\sim$22,500 sh, 17,060 (22), $\sim$12,900 sh, 10,450 (28)
	Solid	$\sim$22,500 sh, 17,100, $\sim$12,700 sh, 10,500
$Ni(IQ)_4(NCS)_2$	Soln.[c]	$\sim$22,500 sh, 17,150 (17), $\sim$12,900 sh, 10,500 (16)
	Solid	$\sim$22,500 sh, 17,150, $\sim$12,900 sh, 10,500
$Ni(py)_4(NCSe)_2$	Soln.[c]	$\sim$22,700 sh, 17,240 (11), 12,770, 10,580 (14)
	Solid	17,240, $\sim$12,800 sh, 10,600
$Ni(\beta\text{-pic})_4(NCSe)_2$	Soln.[c]	$\sim$22,700 sh, 17,180 (12), 12,770, 10,540 (15)
	Solid	17,200, $\sim$12,800 sh, 10,550
$Ni(\gamma\text{-pic})_4(NCSe)_2$	Soln.[c]	$\sim$22,700 sh, 17,240 (14), 12,760, 10,580 (15)
	Solid	17,250, $\sim$12,800 sh, 10,600

[a] Numbers in parentheses represent molar extinction coefficients at band maximum; sh, shoulder. [b] 2.5×10^{-2} M solutions in dried, redistilled, AnalaR nitromethane containing $\sim$5% added amine. [c] 2.5×10^{-2} M solutions in dried AnalaR chloroform containing $\sim$2% added amine.

flectance spectra are reported for the azides because with these decomposition occurred rapidly even in the solid state. In general, from the close agreement of the positions of the absorption bands of the solid state and solution spectra, and the fact that Beer's law is obeyed for the latter, it is concluded that no significant decomposition occurs on dissolution under the conditions used.

The spectra are all of the same general form (see Table II and Figure 1). They consist of three principal bands of relatively low intensity with maxima at 25,000–28,000, 16,000–17,000, and 9700–10,700 cm.$^{-1}$, and two much weaker absorptions at 22,000–23,000 and 12,000–13,000 cm.$^{-1}$. In some cases the highest energy band is not observed or is only poorly resolved because of overlap by the more intense ligand bands, for example those of isoquinoline, NCS, or NCSe. On the basis of the stoichiometry and magnetism of the complexes and the close similarity of their electronic spectra to those of $Ni(py)_4(NCS)_2$ and $Ni(NH_3)_4(NCS)_2$ for which detailed crystal data are available[6] there seems little doubt that all the compounds described here have mononuclear *trans*-octahedral configurations. From the absence of splitting of the 9700 and 16,000–17,000 cm.$^{-1}$ bands we infer that tetragonal distortions arising from the different nature of the ligands, amine and pseudo-halide ion, are small. Accordingly, we have assumed O_h symmetry to be closely approximated and assign the three principal bands to transitions from the $^3A_{2g}$ ground state to the electronic levels $^3T_{2g}(F)$ (ν_1), $^3T_{1g}(F)$ (ν_2), and $^3T_{1g}$(ν_3), and the weak absorptions to spin-forbidden transitions to the singlet states ^1E_g and $^1T_{2g}$.

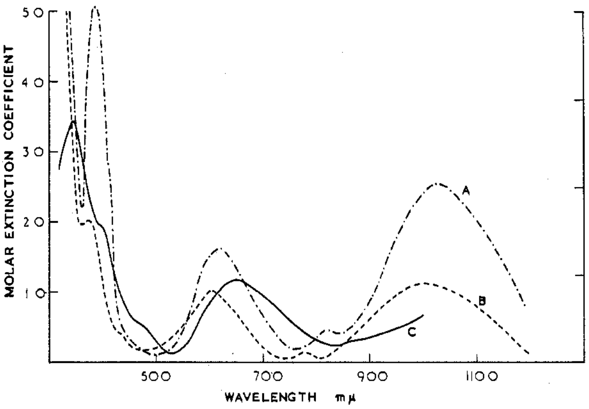

Figure 1.—Electronic absorption spectra of some NiL_4X_2 and NiL_2X_2 complexes: A, solution spectrum of $Ni(py)_4(N_3)_2$; B, solution spectrum of $Ni(py)_4(NCO)_2$; C, diffuse reflectance spectrum of $Ni(py)_2(N_3)_2$. Left-hand scale for curves A and B, right-hand scale for curve C.

Support for a mononuclear six-coordinate configuration, at least for the thiocyanate and selenocyanate complexes, is provided by the infrared spectra. The antisymmetric stretching frequencies of the NCS and NCSe groups fall at 2074 ± 14 cm.$^{-1}$, within the range generally accepted as characteristic of terminal nitrogen coordination.[9]

The ligand field splitting parameter $10Dq$ is taken equal to the energy of the first triplet transition ν_1

(9) P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).

and the Racah parameter B was calculated by substitution of ν_1, ν_2, and ν_3 in the secular equations for the d^8 system.[10] In deriving the ligand field parameters (Table III) only data for the solution spectra were used since in these spectra band maxima could be located more accurately than in the reflectance spectra. The relative uncertainty in $10Dq$ is estimated to be ± 15 cm.$^{-1}$ and that in B to be ± 20 cm.$^{-1}$. As a check on the assumption that tetragonal distortions are small in these complexes one may compare the separation of the ν_2 and ν_3 bands with the value calculated on the basis of O_h symmetry.[7]

TABLE III

CRYSTAL FIELD PARAMETERS FOR NiL_4X_2 COMPLEXES

Complex	$10Dq$, cm.$^{-1}$	B, cm.$^{-1}$	$(\nu_3 - \nu_2)_{calcd} - (\nu_3 - \nu_2)_{obsd}$, cm.$^{-1}$
$Ni(py)_4(N_3)_2$	9,800	840	720
$Ni(\beta\text{-pic})_4(N_3)_2$	9,790	830	560
$Ni(\gamma\text{-pic})_4(N_3)_2$	9,800	840	810
$Ni(IQ)_4(N_3)_2$	9,870	...	...[a]
$Ni(py)_4(NCO)_2$	10,050	880	610
$Ni(\beta\text{-pic})_4(NCO)_2$	10,010	880	650
$Ni(\gamma\text{-pic})_4(NCO)_2$	10,040	880	700
$Ni(IQ)_4(NCO)_2$	10,080	...	...[a]
$Ni(py)_4(NCS)_2$	10,450	860	200
$Ni(\beta\text{-pic})_4(NCS)_2$	10,400	860	360
$Ni(\gamma\text{-pic})_4(NCS)_2$	10,450	860	530
$Ni(IQ)_4(NCS)_2$	10,500	...	...[a]
$Ni(py)_4(NCSe)_2$	10,580	860	540
$Ni(\beta\text{-pic})_4(NCSe)_2$	10,540	850	570
$Ni(\gamma\text{-pic})_4(NCSe)_2$	10,580	860	540

[a] ν_3 band obscured by strong isoquinoline absorption.

Table III shows that $(\nu_3 - \nu_2)_{calcd} - (\nu_3 - \nu_2)_{obsd}$ is relatively small in all cases. Since $(\nu_3 - \nu_2)_{obsd}$ is the difference of two large numbers there is a considerable scatter in the values among the complexes of a given anionic ligand. However, on taking mean values it appears that the tetragonal distortion increases in the order NCS < NCSe < NCO < N_3. When this order is considered in conjunction with the mean $10Dq$ values it is found that pyridine (and its derivatives) occupies a position just below NCS in the spectrochemical series, at least as far as this type of complex is concerned. This is consistent with the value of $10Dq = 10{,}250$ cm.$^{-1}$ for $Ni(py)_6^{2+}$ reported recently by Quagliano and co-workers.[11]

Table III shows that $10Dq$ is dependent both on X and on L. In the case of X the order is NCSe > NCS > NCO > N_3. The Racah parameter B is less sensitive to changes in X. The sequence here is NCO > NCS > NCSe > N_3. The same variations in $10Dq$ and B have been found previously for the tetrahedral CoX_4^{2-} anions.[12]

A much smaller dependence of $10Dq$ on L is observed, and in some cases the variations are within the experimental uncertainty. However, exactly the same sequence, isoquinoline > 4-methylpyridine ~ pyridine > 3-methylpyridine, is found for each pseudo-halide group, indicating that the effect is almost certainly a real one.

NiL_2X_2 Complexes.—In the case of the thiocyanates, selenocyantes, and azides, complexes of this stoichiometry could be prepared by direct reaction of the nickel salt with amine in solution or by heating the solid parent NiL_4X_2 complex either directly or in suspension in a suitable nonsolvent. With the cyanates, however, no definite compounds could be isolated. Thermogravimetric analysis of the mononuclear octahedral $NiL_4(NCO)_2$ series of compounds showed no distinct break corresponding to a composition of $NiL_2(NCO)_2$.

The magnetic moments and diffuse reflectance spectra of the NiL_2X_2 complexes are summarized in Tables I and IV and Figure 1. The moments are characteristic of six-coordinate spin-free nickel(II). The intensities of the spectra are low, as required for a centrosymmetric configuration. The spectral bands are in many cases not resolved because of overlap by the more intense ligand and charge-transfer absorptions. Because of this and the fact that measurements could not be made at frequencies lower than 10,000 cm.$^{-1}$ it was not possible to assign the transitions. However, on the evidence of the stoichiometry, low solubility in organic solvents, magnetism, and low absorption intensities the complexes may be assigned a six-coordinate, probably tetragonal, configuration involving anion bridging. Confirmation for such a structure in the case of the thiocyanates and selenocyanates is provided by the observation that the antisymmetric stretching vibrations of these groups occur at frequencies some 20–40 cm.$^{-1}$ higher than in the corresponding nonpolymeric complexes. Although no correlation of structure with vibrational spectra has yet been made for azido complexes, we find a similar displacement of the antisymmetric stretch of the N_3 ligand toward higher frequencies in the $NiL_2(N_3)_2$ series.

Discussion

It is of interest to consider the origin of the variation in $10Dq$ for the NiL_4X_2 series of complexes. It is generally accepted that the perturbing power of a ligand on metal d-orbitals is a function of at least four effects: (1) purely electrostatic perturbations, (2) the effect of ligand lone pairs, (3) metal-to-ligand π-bonding, and (4) ligand-to-metal π-bonding.[13] Steric effects can also be important in some cases.[14] However, none of the ligands considered here is sterically hindered. Similarly we can neglect (1) as being responsible for variations in $10Dq$ since we are dealing with the same ligand atom in all cases. Nor is there any simple correlation of $10Dq$ with the basic strengths of the ligands. For example, HNCO is said to be a

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[10] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962.

[11] S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

[12] F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961); F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *ibid.*, **83**, 1780 (1961); F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and T. E. Haas, *Inorg. Chem.*, **1**, 565 (1962).

[13] T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960.

[14] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 5042 (1963).

TABLE IV

DIFFUSE REFLECTANCE SPECTRA OF $\mathrm{NiL_2X_2}$ COMPLEXES

Complex	Frequency, cm.$^{-1}$ [a]
$\mathrm{Ni(py)_2(N_3)_2}$	29,000 s, ~25,000 w sh, 21,100 sh, 15,870, 15,380, ~11,500 sh
$\mathrm{Ni(\beta\text{-}pic)_2(N_3)_2}$	29,000 s, 24,800 w sh, 21,100 sh, ~15,870, 15,270, ~11,600 sh
$\mathrm{Ni(\gamma\text{-}pic)_2(N_3)_2}$	29,000 s, ~25,100 w sh, ~20,900 sh, ~15,900, 15,270, ~11,600 sh
$\mathrm{Ni(IQ)_2(N_3)_2}$	~28,600 sh, ~20,900 sh, ~16,000, 15,270, ~11,600 sh
$\mathrm{Ni(py)_2(NCS)_2}$	24,000 sh, 16,500, 13,500 w, 12,000–10,000 unresolved
$\mathrm{Ni(\beta\text{-}pic)_2(NCS)_2}$	28,200 s, 15,300 br, 12,500 w, 12,000–10,000 unresolved
$\mathrm{Ni(\gamma\text{-}pic)_4(NCS)_2}$	28,000 sh, 16,130, 15,500, 12,500 w, 12,000–10,000 unresolved
$\mathrm{Ni(IQ)_4(NCS)_2}$	28,600 s, 16,130, 15,500 sh, 12,500 w, 12,000–10,000 unresolved
$\mathrm{Ni(py)_2(NCSe)_2}$	23,260, 16,530, 13,550

[a] s, strong; w, weak; sh, shoulder; br, broad.

weak acid somewhat stronger than acetic acid and HNCS a strong acid.[15] On this basis $\mathrm{NCO^-}$ would be expected to be a better σ-donor than $\mathrm{NCS^-}$ and therefore to exercise a greater d-orbital perturbation. The opposite is true. Similarly 3-methylpyridine is a better base than pyridine, and 4-methylpyridine better than isoquinoline, as judged by pK_a values,[16] heats of protonation in aqueous solution,[17] and the calculated charge densities on the nitrogen atom,[18] yet the $10Dq$ order bears no relation to these properties. Thus it seems that π-bonding effects must be included in any account of the observed behavior. Since it is true that $10Dq$ increases with metal→ligand π-bonding the most likely explanation is that there is an increasing d_π–p_π overlap in the order $\mathrm{N_3} < \mathrm{NCO} < \mathrm{NCS} < \mathrm{NCSe}$ and also in the order 3-methylpyridine < pyridine ~ 4-methylpyridine < isoquinoline. These are precisely the same conclusions reached from the independent studies of tetrahedral–octahedral configuration equilibria in solutions of the corresponding cobalt(II) complexes, at least as far as the cyanato, thiocyanato, and selenocyanato derivatives are concerned.[3,4,19] (No equilibrium data for the azides are available.) It may be significant, too, that the order for decreasing Racah parameter for the NCO, NCS, and NCSe complexes follows that for increasing $10Dq$. This is the effect expected for increasing d-electron delocalization through metal→amine π-bonding.

Perhaps the most interesting result is the dependence of $10Dq$ on the nature of the heterocyclic aromatic amine. As discussed previously[4] for cobalt(II) complexes the apparently greater π-acceptor capacity of isoquinoline compared to pyridine may be attributed to the more extensive delocalization of the π-electrons in the former. The explanation for the lower $10Dq$ values for 3-methylpyridine complexes compared to those for analogous pyridine or 4-methylpyridine compounds probably lies in the different charge densities and charge distributions in the pyridine ring in the three cases. Since the methyl substituent directs charge into the ring inductively it might be expected that both 3-methyl- and 4-methylpyridine should be less efficient π-electron acceptors than pyridine. Moreover, in 4-methylpyridine the mesomeric effect is such that the 1,3 and 5 positions are those of greatest electron density and the 2,4 and 6 positions those of least electron density. The converse is true of 3-methylpyridine. Similarly, back-coordinated charge from the metal to the pyridine ring will be localized mainly on the 2,4 and 6 positions. These are the same positions that in 3-methylpyridine already carry an excess of charge, so in complexes with this amine back coordination should be inhibited in comparison with 4-methylpyridine complexes, with a consequent reduction in $10Dq$. Thus the π-acceptor capacity should be isoquinoline > pyridine > 4-methylpyridine > 3-methylpyridine. The fact that no difference in $10Dq$ for the pyridine and 4-methylpyridine complexes was observed may be due merely to the smallness of the effect. However, 4-methylpyridine (pK_a = 6.02) is a stronger base at 25° than pyridine (pK_a = 5.17)[16] and it is not unlikely that the greater availability of the σ-bonding electrons in the former compensates for the smaller π-contribution.

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