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An Analysis of the Electronic Spectra of Some Nickel(II) Halide Amine Complexes

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The diffuse reflectance spectra (30,000–10,000 cm.⁻¹) of 28 six-coordinate nickel(II) complexes of microsymmetry NiN₂X (N = amine, X = Cl or Br) are analyzed in terms of octahedral stereochemistry. It is shown that the rule of average environment is not generally applicable as far as these compounds are concerned. The derived effective crystal field splitting energy (10Dq') of the amine is frequently greater in the bromo than in the chloro complexes, and the ratio 10Dq' (bromide)/10Dq' (chloride) is correlated with the expected relative degree of metal→amine π -bonding. Sterically hindered amines are found to give rise to low 10Dq values. No simple relationship between 10Dq' and pK_a of an amine is apparent, even for non- π -acceptor amines.

Introduction

There has been considerable interest during the past few years in complexes formed between amines and nickel(II) salts, particularly with regard to stereochemistry. As a result a large number of six-coordinate nickel(II) amine complexes have now been characterized.^{2–7} Although in many cases detailed electronic spectral data were cited few theoretical studies have been published.^{2,8–10}

In this paper we discuss the electronic spectra of complexes of the type Ni(amine)₂X₂ (X = Cl or Br) in which six-coordination of the metal atom is achieved by halide bridging. The spectra and other properties of most of the complexes considered here have been reported previously.^{3–7} However, a number of new complexes are also included.

Experimental

Preparation of Complexes.—The complexes with aniline and *m*- and *p*-toluidine have not been previously reported. For the aniline and toluidine chloro compounds, hot ethanolic solutions of the hydrated nickel halide (1 mole) were added dropwise with stirring to hot ethanolic solutions of the appropriate amine (2 moles). The pale green products which settled out on cooling were washed with warm ethanol containing a little of the amine, followed by carbon tetrachloride, and then filtered and dried in a desiccator. With all the other complexes the above procedure yielded either the tetrakis amine complex or mixtures of the tetrakis and bis compounds. Pure samples of the latter were obtained by refluxing the initial product at least twice with either chloroform or benzene, followed by filtration of the hot suspension and washing with carbon tetrachloride.

Analyses.—The compounds were analyzed for nickel by EDTA titration in ammonia–ammonium chloride buffer at ~30° using murexide indicator. The analytical results are given in Table I.

Diffuse Reflectance Spectra.—The diffuse reflectance spectra were measured with a Hilger Uvispek Type H700 spectrophotometer, fitted with a reflectance attachment (Type H740).

Magnetic Moments.—Magnetic moments were determined by the Gouy method at 17–19°. Hg(NCS)₄Co was used as calibrant. Diamagnetic corrections were applied in all cases, and the moments were calculated assuming the Curie law.

Calculation.—The calculation assumed the following energies.¹¹

$$E(^3A_{2g}) = -12Dq \quad E(^3T_{1g}, F) \text{ and } E(^3T_{1g}, P)$$

$$\begin{vmatrix} 8Dq + 3B - E & 6B \\ 6B & -2Dq + 12B - E \end{vmatrix} = 0$$

The secular equation was solved with the aid of the Atlas Computer of the University of Manchester. The authors are especially indebted to Dr. J. Lee for devising the program.

Results and Discussion

Table II lists the magnetic moments and diffuse reflectance spectral bands for the previously uninvestigated complexes. The low intensities of the spectra indicate a centrosymmetrical configuration and the stoichiometry, magnetic moments, and positions of the spectral bands are all consistent with the same polymeric octahedral or tetragonal structure previously proposed for the other complexes.^{3–7}

Although formally of D_{4h} symmetry, with microsymmetry NiN₂X₄, all 28 complexes considered in this paper have spectra, at least in the range 30,000–10,000 cm.⁻¹, typical for octahedrally (O_h) coordinated nickel(II). The comparatively high magnetic moments of this class of compound have already been briefly discussed.¹² In the related mononuclear complexes of the type NiL₄X₂, there is evidence for a greater degree of tetragonality.^{7–9} However, in the complex Ni(NH₃)₄(NO₂)₂, where tetragonal distortion is large enough to be detected spectroscopically, the splitting of the various excited states is only of the order of a few hundred wave numbers.⁸ We therefore feel justified in the absence of any abnormal splitting of the two visible absorption bands, and for the purposes of the present analysis, to make the approximation that

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TABLE I
 ANALYTICAL DATA FOR SOME Ni(amine)₂X₂ COMPLEXES

	% Ni			% Ni	
	Calcd.	Found		Calcd.	Found
Ni(aniline) ₂ Cl ₂	18.6	18.5	Ni(isoquinoline) ₂ Br ₂	12.3	12.3
Ni(aniline) ₂ Br ₂	14.5	14.5	Ni(<i>o</i> -toluidine) ₂ Cl ₂	17.1	17.1
Ni(3-ethylpyridine) ₂ Cl ₂	17.1	17.0	Ni(<i>o</i> -toluidine) ₂ Br ₂	13.6	13.6
Ni(3-ethylpyridine) ₂ Br ₂	13.6	13.6	Ni(<i>p</i> -toluidine) ₂ Cl ₂	17.1	17.1
Ni(isoquinoline) ₂ Cl ₂	15.1	15.1	Ni(<i>p</i> -toluidine) ₂ Br ₂	13.6	13.6

 TABLE II
 DIFFUSE REFLECTANCE SPECTRA AND MAGNETIC MOMENTS OF SOME NICKEL(II) AMINE COMPLEXES

Complex	χ_M^a	μ^b	Absorption spectra, cm. ⁻¹			
Ni(3-ethylpyridine) ₂ Cl ₂	4661	3.37	23,580	21,740 sh	13,420	11,630 sh
Ni(3-ethylpyridine) ₂ Br ₂	4723	3.40	23,000	18,870 sh	12,970	10,990 sh
Ni(isoquinoline) ₂ Cl ₂	4784	3.40	24,100	22,730 sh	13,910	12,270 sh
Ni(isoquinoline) ₂ Br ₂	4820	3.42	23,420	21,740 sh	13,640	11,490 sh
Ni(aniline) ₂ Cl ₂	4725	3.36	23,260	19,610 sh	13,760	11,830 sh
Ni(aniline) ₂ Br ₂	4747	3.39	22,470	18,520 sh	13,230	11,630 sh
Ni(<i>m</i> -toluidine) ₂ Cl ₂	4787	3.41	23,260	19,610 sh	13,790	11,830 sh
Ni(<i>m</i> -toluidine) ₂ Br ₂	4708	3.39	22,470	18,520 sh	13,250	11,630 sh
Ni(<i>p</i> -toluidine) ₂ Cl ₂	4845	3.43	23,310	19,340 sh	13,810	11,900 sh
Ni(<i>p</i> -toluidine) ₂ Br ₂	4745	3.42	22,570	18,520 sh	13,260	11,630 sh

^a Uncorrected molar susceptibility in c.g.s. units. ^b Bohr magnetons at 17–19°. Bands listed in the first and third columns are assigned to the ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ and ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transitions, respectively. Data in the second column correspond to a triplet-singlet transition. The band in the fourth column may also be triplet-singlet in character, but could be a component of the nearby spin-allowed band.

the maxima of these two bands closely correspond to the transitions ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(\gamma_2)$ and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(\gamma_3)$ in octahedral symmetry. Certain of these complexes have been studied very recently by Goodgame, *et al.*¹³ These authors assign the shoulders on the ν_2 and ν_3 bands as spin-allowed transitions to components of the ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ levels in D_{4h} symmetry; splittings of the order of 1000–2000 cm.⁻¹ were therefore assumed to occur in these levels. Such large splittings are unlikely. The splitting of the $T_{1g}(F)$ level is predicted to be the inverse of that of the $T_{1g}(P)$ level^{12,14}; since these states interact very strongly, the net splitting in D_{4h} symmetry is likely to be small (certainly less than 1000 cm.⁻¹). We prefer to assign the shoulders, when they occur, to spin-forbidden transitions, in line with earlier studies.^{11,14} Accordingly, from the observed positions of ν_2 and ν_3 we have calculated the ligand field parameters $10Dq$ and B (Racah parameter) by use of the secular equations for the d^8 system¹¹ (see Experimental section). The calculation includes the mutual interactions between the T_{1g} levels, but ignores spin-orbit coupling. The mean $10Dq$ and B values, summarized in Table III, refer to the excited states concerned rather than to the ground state of the ion. With the exception of the new complexes listed in Table II, the spectral data used for the calculations were taken from the literature.^{3–5,7} By application of the "average environment rule"^{2,15} we have also calculated the apparent crystal field splitting energies of the amines themselves. For this purpose the literature values¹¹ for $10Dq$ of 7200 and 7000 cm.⁻¹ for the chloride and bromide ion, respectively, were assumed.

These data are given in Table IV along with values of the ratio (R) of $10Dq'$ in the bromides to $10Dq'$ in the chlorides. Published pK_a values¹⁶ of the amines are collected in column 5 of Table IV.

 TABLE III
 THE MEAN CRYSTAL FIELD STRENGTH ($10Dq$) AND RACAH PARAMETER (B) OF THE COMPLEXES Ni(amine)₂X₂ (CM.⁻¹)

Amine ^a	Mean $10Dq$ B (chlorides)	Mean $10Dq$ (bromides)	B	ref.
3-Methylpyridine	8600 820	8370	800	7
4-Methylpyridine	8540 830	8430	800	7
Pyridine	8500 840	8420	810	7
<i>p</i> -Toluidine	8460 790	8100	770	<i>b</i>
<i>m</i> -Toluidine	8450 780	8100	760	<i>b</i>
Isoquinoline	8450 850	8345	810	<i>b</i>
Aniline	8420 790	8020	770	<i>b</i>
Acetonitrile	8315 830	8690	729	<i>d</i>
2,6-Dimethylpyrazine	8150 860	8210	800	4
Ammonia	8140 930	7850	890	7
3-Ethylpyridine	8090 870	7890	830	<i>b</i>
Quinoline	7990 790	(Tetrahedral)		3
Methylpyrazine ^c	7950 820	8150	800	4
2,5-Dimethylpyrazine ^c	7860 810	(Square)		4
Quinoxaline ^c	7810 880	7810	890	5

^a Listed in decreasing order of $10Dq$ in the chloro series.
^b This work. ^c Empirical formula $NiLX_2$ with bridging amine as well as bridging halogen. ^d B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, 2400 (1964).

From an examination of the data in Tables III and IV, four main conclusions may be drawn: (a) The relative order of the amines in the spectrochemical series computed from the spectra of the chloro complexes is different from that computed from the spectra of the bromo complexes. In some cases $10Dq$ increases on passing from the chloride to the bromide, in others a

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TABLE IV
AMINE CRYSTAL FIELD STRENGTHS ($10Dq'$) COMPUTED FROM THE
AVERAGE ENVIRONMENT RULE (CM.⁻¹)

Amine ^a	$10Dq'$ (chlorides)	$10Dq'$ (bromides)	R^b	pK_a^{18}
Acetonitrile	10,550	12,070	1.14	
Methylpyrazine ^c	9,450	10,450	1.11	1.48
2,6-Dimethylpyrazine	10,050	10,630	1.06	2.64
Quinoxaline ^c	9,030	9,430	1.04	0.72
2,5-Dimethylpyrazine ^c	9,180	...	...	2.04
Pyridine	11,100	11,260	1.01	5.23
4-Methylpyridine	11,220	11,290	1.01	6.02
Isoquinoline	10,950	11,040	1.01	5
Quinoline	9,570	...	...	4.94
3-Methylpyridine	11,400	11,100	0.97	5.68
3-Ethylpyridine	9,870	9,670	0.98	5.56
Ammonia	10,020	9,550	0.95	9.27
<i>m</i> -Toluidine	10,950	10,300	0.94	4.67
<i>p</i> -Toluidine	10,980	10,300	0.94	5.07
Aniline	10,860	10,060	0.93	4.58

^a Listed in decreasing order of R . ^b Ratio $10Dq'$ (bromide) to $10Dq'$ (chloride). ^c See Table III.

decrease occurs. (b) There is no simple relationship between the pK_a of an amine and its crystal field splitting parameter. (c) The Racah parameter B is relatively insensitive to both amine and halogen. (d) Sterically hindered ligands give rise to lower crystal field splitting energies.

The variation in the apparent crystal field splitting energies of the amines with the nature of the halide shows that the average environment rule is not generally applicable to these complexes. For this to hold the ratio R should be unity in all cases. The average environment rule may be expected to be valid if the bonding is essentially electrostatic. We may expect deviations if covalent bonding, particularly π -bonding, occurs. Nevertheless, the rule has been used in many studies¹⁷ with compounds which could hardly be called ionic. Breakdown of the rule as indicated from spectroscopic studies, especially in the solid state, could arise through various mechanisms such as steric hindrance and crystal packing effects. However in a study of a wide range of different amines, these effects might well be assumed to operate in a random manner. We prefer therefore to attribute the orderly behavior of the ratio R to a definite phenomenon, namely, π -bonding. We assume that the breakdown of the rule is due to a variation in the $10Dq$ of the amines, rather than in a variation of $10Dq$ of the Cl^- or Br^- ion, because this seems a more reasonable assumption than the reverse and because there is evidence that the crystal field strength of a halide ion is fairly constant (e.g., bridging and terminal halides have similar or identical crystal field strengths).^{14,18}

In view of the fact that the complexes do not have strict octahedral symmetry, we attach significance only to the relative magnitudes of R , not to the absolute values. It can be seen (Table IV) that the R

values span the range 0.93 to 1.14. The reason why $10Dq$ for the amine is frequently greater in the bromides than in the chlorides can perhaps best be explained in terms of back donation from metal to amine. On replacement of chloride ion by the less electronegative bromide ion more negative charge is released onto the metal atom thereby enhancing the overlap of the metal t_{2g} orbitals with vacant π -acceptor amine orbitals. Since the crystal field splitting is sensitive to metal-ligand π -bonding,¹⁹ the effect is to raise the effective $10Dq$ of the amine in the bromide series, the t_{2g} orbital energy being reduced by partial delocalization over the amine. The mechanism is analogous to that used to explain the variation in infrared stretching frequency of the CO group in substituted carbonyl complexes,²⁰ as has been suggested previously in a discussion of the pyrazine compounds.¹⁰ Thermodynamic evidence for increasing metal pyridine back donation in mononuclear $Co(pyridine)_4X_2$ complexes in the sequence $X = Cl < Br < I$ has been presented previously.²¹ Although such π -bonding effects are likely to be less striking in complexes containing bridging halogen,⁷ they are probably still significant. In general, the experimental results and the parameters derived therefrom seem to bear this out. Thus for complexes with ammonia, aniline, or the toluidines which do not possess any suitable π -acceptor orbitals, the ratio R is smallest (0.93–0.95). Again, for the pyrazine group of complexes in which the planar pyrazine rings have π -antibonding orbitals of appropriate symmetry for overlap with occupied nickel t_{2g} orbitals, the ratio R is the greatest (1.04–1.11). Pyridine and its derivatives, of course, also have available π -acceptor orbitals and evidence for a moderate degree of π -bonding in six-coordinate cobalt pyridine complexes has already been reported.²¹ However the degree of metal-amine back donation in pyridine complexes is probably less than in pyrazine complexes since attack by nucleophilic reagents is easier with pyrazines,²² i.e., the pyrazine ring has a low electron density. In accord with this view of the relative π -acceptor capacities of the pyridines and pyrazines we find that R falls in a lower range for complexes of the former group of amines.

It is interesting that R is smaller for complexes with 3-alkyl-substituted pyridines than for those with pyridine itself or with 4-substituted pyridines. In terms of the proposed correlation between R and the degree of back donation, this suggests that the 3-alkyl-substituted pyridines are poorer π -acceptors. There are two independent lines of support for this view. First, the results of a thermodynamic study of configuration equilibria in chloroform solutions of analogous $Co(II)$ complexes indicate that octahedral CoL_4X_2 complexes ($X = Cl, Br, NCS$) are substantially less

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stable (relative to tetrahedral CoL_2X_2) where $\text{L} = 3$ -methylpyridine than when $\text{L} = \text{pyridine}$, 4-methylpyridine, or isoquinoline.²³ Second, values of $10Dq$ for mononuclear six-coordinate Ni(II) complexes, NiL_4X_2 ($\text{X} = \text{NCO}$, NCS , NCSe , and N_3), are consistently smaller for $\text{L} = 3$ -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

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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

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

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The electronic spectra and magnetic moments for a series of complexes NiL_4X_2 are reported ($\text{L} = \text{pyridine}$, 3-methylpyridine, 4-methylpyridine, or isoquinoline; $\text{X} = \text{NCO}$, 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, $\text{NCSe} > \text{NCS} > \text{NCO} > \text{N}_3$ and $\text{NCO} > \text{NCS} > \text{NCSe} > \text{N}_3$. 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 ($\text{X} = \text{NCS}$, 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 $\rightarrow$ X

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