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Ligand Field Spectra of Hydrazine Complexes of Ni^{II}, and the Spectrochemical Position of Hydrazine

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Solid nickel(II)-hydrazine complexes, $Ni(N_2H_4)_2X_2$ and $Ni(N_2H_4)_3X_2$, have ligand-field spectra corresponding to those expected for [trans–NiN_4X_2] and [NiN_6] chromophores respectively. This contrasts with solution spectra of hydrazine complexes, where hydrazine is often unidentate and is often only partially substituted in the coordination sphere. The present study thus affords a unique occasion to establish the spectrochemical properties of the hydrazine ligand. The spectrochemical position of hydrazine is practically coincident with that of other diamines, and higher than that of, say, ammonia. The axial field strength is unusually low, and the nephelauxetic ratio unusually high in the trans-*disubstituted octahedral chromophores [NiN_4X_2]. These data imply that (in these complexes) hydrazine can acquire a conformation which is particularly favorable for the formation of stable σ bonds, and that the axial field is particularly weak, thus implying weak σ-covalent character of the axial bonds and hence poor σ-delocalization and low nephelauxetic effect.*

Introduction

Among the diamine ligands $H_2N–(CH_2)_n–NH_2$, the $n = 0$ term, *i.e.* hydrazine, is much less known in its spectrochemical behaviour than ethylenediamine and the higher terms, although it is generally recognized that hydrazine is a good donor towards metals. A possible reason for this is that hydrazine does not always act as a bidentate ligand to the same metal center[1,2,3,4] this prevents direct comparison with ethylenediamine and its higher homologues, made more difficult by the fact that hydrazine complexes are often highly polymeric, hence insoluble and not amenable to absorption-spectroscopic investigation. Data hitherto available on the spectrochemical behaviour of hydrazine are rather scattered; *e.g.* Fe^{II} salts in anhydrous hydrazine[5] are probably present as $[Fe(N_2H_4)_6]^{2+}$ containing monodentate hydrazine, and having $\Delta = 11.84$ kK (compare $\Delta = 10.50$ kK for $[Fe(H_2O)_6]^{2+}$ and $\Delta = 11.15$ kK for $[Fe(NH_3)_6]^{2+}$).[5,6] It is clear from these and other scattered data[7,8,9] that hydrazine has a rather high ligand field strength, comparable, if not higher than, that of other amino ligands. On the whole however the spectrochemical behaviour of hydrazine has not been widely investigated.

We report the spectra of complexes of Ni^{II} with hydrazine of the general formulas $Ni(N_2H_4)_2X_2$ (X = Cl, Br, I, NCS) and $Ni(N_2H_4)_3X_2$ (X = Cl, Br, NO_3, $\frac{1}{2}SO_4$, BF_4). These are highly insoluble and, by comparison with the analogous $M^{II}(N_2H_4)_2X_2$ and $M^{II}(N_2H_4)_3X_2$ complexes (M^{II} = Co, Zn, Mn),[2,3,11] should possess polymeric structures based on a three-dimensional network of metal-hydrazine chains for the *tris*-hydrazine complexes, or linear bis-(μ-hydrazine)-metal chains for the bis-hydrazine complexes.[3,11,12] The structure is far better known for bis- than for tris-hydrazine complexes,[2,3] but in either case the structures are likely to involve bridges of bidentate hydrazine.

We have measured the reflectance spectra in the solid state, which appears to be the only technique capable of providing information on the spectra of complexes containing chelated hydrazine, since solution species are often only partially hydrazinated and probably contain monodentate hydrazine.[7]

Since reasonable assumptions may be made as to the composition and geometry of the involved chromophores, the spectral results enable us to establish the spectrochemical position of hydrazine, this is practically coincident, or even slightly higher than, that of ethylenediamine. It is also possible to check the applicability of the ligand-field computational schemes to complexes like $Ni(N_2H_4)_2Cl_2$, $Ni(N_2H_4)_2Br_2$ and $Ni(N_2H_4)_2I_2$ which exhibit one of the strongest degrees of tetragonality observed with *trans*-disubstituted pseudooctahedral complexes of high-spin Ni^{II}.

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Table I. Reflectance spectra of nickel-hydrazine complexes

Solid	ν_1 (kK) $\rightarrow{}^3T_{2g}$ (Oh)		ν_2 (kK) $\rightarrow a\,{}^3T_{1g}$ (Oh)		ν_3 (kK) $\rightarrow b\,{}^3T_{1g}$ (Oh)	
	$\rightarrow a^3E_g$	$\rightarrow B_{2g}$ (D_{4h})	$\rightarrow a^3A_{2g}$	$\rightarrow b^3E_g$	$\rightarrow b^3A_{2g}$	$\rightarrow c^3E_g$
$Ni(N_2H_4)_3Cl_2$	11.6_0		18.5_0		29.2	
$Ni(N_2H_4)_3Br_2$	11.7_0		18.6_0		29.1	
$Ni(N_2H_4)_3SO_4$	11.7_0		18.5_5		29.0	
$Ni(N_2H_4)_3(NO_3)_2$	11.6_5		18.4_5		29.2	
$Ni(N_2H_4)_3(BF_4)_2$	11.6_2		18.5_1		29.4	
$Ni(N_2H_4)_2Cl_2$	8.1_5	11.6_0	14.25	17.0_5	26.0	27.0
$Ni(N_2H_4)_2Br_2$	7.9_0	11.7_0	13.6_0	16.6_0	26.0	26.9
$Ni(N_2H_4)_2I_2$	7.7_5	11.62	13.24	16.33	26.6_6	
$Ni(N_2H_4)_2(NCS)_2$	10.7_8	11.60	17.9_0		28.3_5	

Experimental Section

Preparation of complexes. The complexes $Ni(N_2H_4)_3X_2$ (X = Cl, Br, NO_3, $\frac{1}{2}SO_4$, BF_4) were obtained by reacting 1 mole of the corresponding hydrated nickel salt with 10 moles of 80% aqueous hydrazine in ethanol at room temperature. The yields were nearly quantitative.

The complexes $Ni(N_2H_4)_2X_2$ (X = Cl, Br, I, NCS) were prepared by reacting 1 mole of the nickel salt with 1 mole of 80% aqueous hydrazine in ethanol at room temperature (yield about 50%).

$Ni(N_2H_4)_3(BF_4)_2$ (Found: Ni 17.7, N_2H_4 29.7; $H_{12}B_2F_8N_6Ni$ requires: Ni 17.9, N_2H_4 29.2) has not previously been isolated; all other complexes have already been prepared by different methods.[13,13',14,15,16]

Spectral measurements. The reflectance spectra were measured with a Beckman DK/2 spectrophotometer, using a standard reflectance attachment and magnesium oxide as the reference.

Results and Spectrochemical Parameters

Tris-hydrazine complexes. The spectra of $Ni(N_2H_4)_3X_2$ (X = Cl, Br, NO_3, $\frac{1}{2}SO_4$, BF_4) are always the same, irrespective of the nature of X, and follow the spectral patterns typical of octahedral Ni^{II} complexes. Spectral data, as exemplified in Figure 1 and listed in Table I, are consistent with $\Delta(=\nu_1) = 11.7$ kK, and $B = 0.910$ kK ($\beta = 0.885$). It is to be noted that spectral frequencies and parameter values are fairly close to those of tris(ethylenediamine)-nickel(II), thus suggesting substantial similarity of spectrochemical behaviour between hydrazine and other polymethylenediamines.

Bis-hydrazine complexes. The spectra (see Figure 1 and Table I) show remarkably large splitting of the ν_1 and ν_2 bands, indeed the amount of tetragonality exhibited by these substances is among the highest observed to date in $Ni^{II}A_4B_2$ type complexes higher *e.g.* than Ni^{II} (pyridine)$_4X_2$, and comparable to Ni^{II}(benzimidazole)$_4X_2$ (X = Cl, Br).[17]

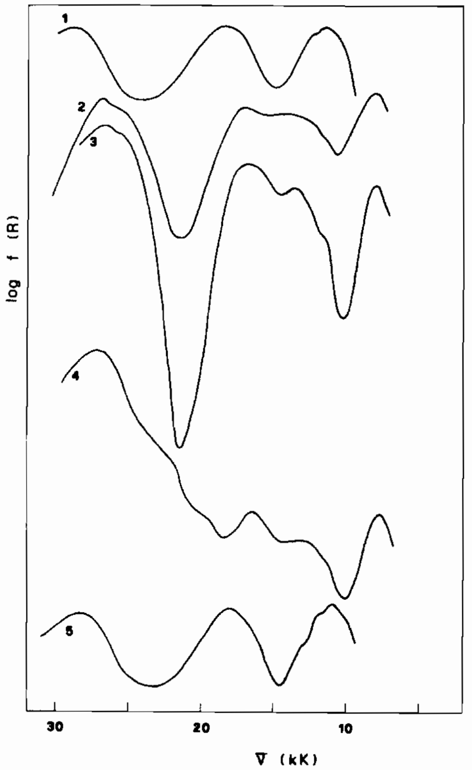

Figure 1. Reflectance spectra of solid nickel-hydrazine complexes: 1 $Ni(N_2H_4)_3Cl_2$; 2 $Ni(N_2H_4)_2Cl_2$; 3 $Ni(N_2H_4)_2Br_2$; 4 $Ni(N_2H_4)_2I_2$; 5 $Ni(N_2H_4)_2(NCS)_2$.

One of the components of ν_1 falls almost exactly at the same frequency as ν_1 in the tris-hydrazine complexes, as is demanded by the ligand field scheme for axial distortions.[17] The frequency of the low-energy component of ν_1 also depends, on the other hand, on the strength of the axial ligands. Evaluation of the frequency data of the split terms of ν_2 and (although often much less evident) of ν_3 allows determination of the spectral parameter values of the tetragonal field according to the current computational schemes.[17]

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Table II. Spectral parameter values (in kK) of octahedral and tetragonal nickel-hydrazine complexes

Complex	$[Ni(N_2H_4)_3X_2]$ [a]	$[Ni(N_2H_4)_2Cl_2]$		$[Ni(N_2H_4)_2Br_2]$		$[Ni(N_2H_4)_2I_2]$		$[Ni(N_2H_4)_2(NCS)_2]$	
Chromophore	$[Ni^{II}N_6]$	$[Ni^{II}N_4Cl_2]$		$[Ni^{II}N_4Br_2]$		$[Ni^{II}N_4I_2]$		$[Ni^{II}N_4N_2]$	
		I	II	I	II	I	II	I	II
Dq_N	1.16	1.16	1.16	1.17	1.17	1.16	1.16	1.16	1.16
Dq_X	—	.47	.46	.41	.405	.39	.38	$.99_4$	1.00
Dt	—	$.39_4$	.49	.43	.43	.44	.45	$.09_4$	0.9_3
Ds	—	.55	.78	.59	.76	.61	.49	$.02_0$	—.12
Δ_1	—	—.32	.35	—.40	.10	—.37	—.78	—.41	—.82
Δ_2	11.60	11.60	11.60	11.70	11.70	11.62	11.62	11.60	11.60
Δ_3	—	4.17	5.37	4.53	5.18	4.64	4.23	.55	—.02
$d\sigma$	—	—1.56	—1.92	—1.70	—1.90	—1.74	—1.58	—.21	.01
$d\pi$	—	.16	—.17	.20	—.05	.19	.39	.20	.41
$e_{\sigma N}$	3.87	3.87	3.87	3.90	3.90	3.87	3.87	3.87	3.87
$e_{\sigma X}$	3.87	1.79	1.31	1.63	1.30	1.55	1.77	3.59	3.81
$e_{\pi X}-e_{\pi N}$	—	.16	—.17	.20	—.05	.19	.39	.20	.41
B	$.86_5$	$.96_3$	$.99_6$	$.95_7$	1.00_6	1.00_4	1.00_1	$.89_1$	.87
β	.84	.93	.96	.93	.97	.96	.96	.86	.84

[a] X = Cl, Br, NO_3, ½SO_4, BF_4 (average) I = Weak field tetragonal scheme II=Strong field scheme with complete configuration interaction.

Table II lists the parameter values determined from the experimental data according to two schemes, *i.e.* (i) tetragonal perturbation superimposed on the weak-field octahedral terms, and (ii) complete configuration interaction in the strong-field formalism (C.I.). The results of the two computations are not exactly coincident, probably owing to limited accuracy in the identification of the true centers in the somewhat unresolved experimental spectra.

In the weak-field tetragonal scheme the in-plane ligand field strength Dq_N is obtained as $\frac{1}{10}\nu(^3B_{2g})$, while Dq_x is $\frac{1}{10}(2\nu(^3E_g)-\nu(^3B_{2g}))$; the tetragonality parameters Ds and Dt are given as $Dt = \frac{4}{35}(\nu(^3B_{2g})-\nu(a^3E_g))$, and $Ds = \frac{1}{6}(\nu(b^3E_g)-\nu(a^3A_{2g})+\frac{5}{4}Dt)$ respectively. The strong-field tetragonality parameters Δ_1 and Δ_3 (Δ_2 being 10 Dq_N) are given in the same scheme as $\Delta_1 = E(xy)-E(xz\,.\,yz) = 3Ds-5Dt$ and $\Delta_3 = E(x^2-y^2)-E(z^2) = 4Ds+5Dt$; $d\sigma$ and $d\pi$, the parameters of the molecular orbital treatments by Yamatera[15] and McClure,[16] are calculated as $d\sigma = -\frac{3}{8}\Delta_3$, $d\pi = -\frac{1}{2}\Delta_1$.

The corresponding values of the angular overlap parameters[23] are calculated as $e_{\sigma N} = \frac{10}{3}Dq_N = \frac{1}{3}\nu(^3B_{2g})$, $e_{\sigma x} = e_{\sigma N}+\frac{4}{3}d_\sigma$, $e_{\pi x} = d\pi$ ($e_{\pi N}$ is assumed to be zero because of the negligible ability of amine nitrogen to form coordinative π-bonds).

A quite different type of evaluation was followed in strong-field C.I. method, yielding Δ_1 as $\Sigma_j\nu(j^3E_g)-\Sigma_j\nu(j^3A_{2g})-\Delta_2$, B being evaluated either from the differences of the octahedral limits $R_\mp$ of the ν_2 and ν_3 bands through $(R_+-R_-)^2 = 225B^2+\Delta^2-18B\Delta$ or from the relation $R_++R_- = 3\Delta_2+15B = \Sigma\nu(A_{2g})+2Ds+20Dt$.

There follows, in the logical procedure of parameter evaluation, $\Delta_3 = \Delta_1+1.5\Delta_2-\frac{1}{2}\Sigma\nu(^3A_{2g})+7.5\,B$, while $d\sigma$ and $d\pi$ are calculated from Δ_3 and Δ_1 as above, $Dt = \frac{1}{35}(3\Delta_3-4\Delta_1)$ and $Ds = \frac{1}{7}(\Delta_1+\Delta_3)$.

The data obtained according to the two computational schemes are reported in Table II. The shapes of the experimental spectra exhibit a good qualitative agreement with the previsions of both schemes whereas a certain amount of ambiguity persists about the quantitative agreement.

This is due primarily to the uncertainty in the attribution of the bands, particularly of that at 13-14 kK which could be the spin-forbidden transition $^1E_g\leftarrow$, whereas the spin-allowed component $^3A_{2g}\leftarrow$ could be hidden in the unresolved envelope. This attribution is supported by the fact that the tetragonal splitting of the band $a^3T_{1g}\leftarrow$ is generally small, whereas in our case its value is about 3 kK. However the large splitting observed is formally compatible with either computational scheme, especially with the second, which takes account of configuration interactions between the levels derived from the two octahedral terms $^3T_{1g}\leftarrow$. We shall discuss the results on the basis of the tentative attribution as $^3A_{2g}\leftarrow$. As mentioned further uncertainties, derive from the bad resolution of the spectra and result in parameter values (expecially tetragonality parameters) uncertain and dependent on the method. This obviously limits the meaning of these parameters, although some general tendencies are evident. In the next section we shall try to discuss their chemical meaning.

Discussion

Tris(hydrazine)-complexes. The Δ values is practically coincident with that of other diamine ligands, and, also, the β value, being slightly lower than 1, is close to that of ammonia and of amine ligands. These data suggest that the spectrochemical behaviour of hydrazine in complexes is quite similar to that of other diamine ligands, even if hydrazine, owing to its configuration, is not able to act as a bidentate ligand to the same metal center. In fact bidentate hydrazine is rather a bridging ligand.

The high β value undoubtedly reflects the low tendency of amine nitrogen to promote π-delocalization in either sense, and the high Δ value points to a situation where hydrazine in its bridging form achieves a conformation where it presents its lone pairs of nitrogen in the most favorable situation for strong σ coordinative bonding. This has been confirmed by direct X-ray structure determination in the case of chains of bis(μ-hydrazine)-metal complexes of Zn,[12,20] Cd[20] and Mn.[11]

Bis(hydrazine)-complexes. As noted above, the spectra of these species are consistent with the expectation for pseudooctahedral [*trans*–$Ni^{II}N_4X_2$] chromophores of practically D_{4h} symmetry. Tetragonality effects are, as discussed previously, particularly relevant in the present case, which can be regarded as typical of strongly pronounced tetragonality in nickel(II) complexes with simple ligand geometry.

The ligand field strength of hydrazine ligands is practically unchanged from the tris-(hydrazine)-complexes, Δ ranging between 11.6 and 11.7 kK. Instead, the axial field strength, as given by Dq_z, is distinctly lower than would be expected considerating the known σ and π antibonding ability of the involved ligands, or of the know spectrochemical behaviour of the corresponding purely octahedral chromophores. Thus, for $X = Cl$, Dq_z is in the range 0.45 kK, $e_{\sigma Cl}$ in the range 1.55, for $X = Br$, $Dq_z \sim 0.40$, $e_{\sigma Br} \sim 1.40$, and for $X = I$, $Dq_z \sim 0.38$, $e_{\sigma I} \sim 1.66$, which would imply ligand field strengths $\Delta \sim 4.5$, $\Delta \sim 4.0$ and $\Delta \sim 3.8$ kK for the corresponding [$Ni^{II}X_6$] chromophores.

These values are significantly lower than the experimental values for the actual [$Ni^{II}Cl_6$] or [$Ni^{II}Br_6$] chromophores as present *i.e.* in the corresponding anhydrous nickel halides, which are of the order of 7.2 kK for Cl, or 7.0 kK for Br.[21] The ligand field strength of I in the chromophore [$Ni^{II}I_6$] should be, presumably, of the same order.

In the case of the thiocyanate complex, Dq_z is about 1.0 kK, *i.e.* $\Delta_{(NCS)} \sim 10$, which agrees with the value $\Delta_{(NCS)} = 9.6$ kK reported for the complex [$Ni(NCS)_6$][10] but is lower than the value $\Delta_{(NCS)} = 11.0$ evaluated for the *trans*-tetragonal complex $Ni(NH_3)_4(NCS)_2$.[14]

Comparing this with the latter results, we can argue that also there is a slight weakening effect in the axial ligand field strength in the case of [$Ni(N_2H_4)_2(NCS)_2$].

Generally, to weak axial ligand-field strengths are expected in those cases where the equatorial ligands exert a strong steric hindrance, preventing axial ligands from approaching the central metal as closely as would be required for optimum covalent bonding.[17] However, if the structure is as ascertained for $Mn(N_2H_4)_2Cl_2$ and similar cases,[11,12] no particular steric hindrance should be exerted by equatorial hydrazine molecules, as is reasonable with a non-bulky ligand like hydrazine. There are, in what are the known or presumed structures of there complexes, no clear hints as to the possible reason for this unusually low spectrochemical effect of the axial ligands. Working in the current interpretive schemes, this fact would strongly suggest that, owing possibly to packing effects in the lattice, the axial ligands are relatively far from the nickel atoms, thus weakening both the σ and (in part) the π bonds.

As indirect support for this view, may perhaps be seen in the B values, which, even if determined through different reckoning schemes, are invariably unusually large, in particular larger than in the tris-(hydrazine)-complexes. This trend is also evident in the fairly high position of the group of the ν_3 frequencies ($\sim$29 kK), which is the highest value observed among octahedral or pseudooctahedral nickel(II) complexes.[21]

Values of β in the range ~ 1.0 are not consistent with any average estimate of the nephelauxetic effect for the involved ligands and, unless one accepts complete breakdown of any ligand field model, may be rationalized on the assumption that the coordinate bonds are, as far as the axial positions are concerned, very weakly covalent, leading to small intermixing of the electronic systems of the central atom and of the ligands, and this in turn should correspond to unusually long bond lengths.

This view could perhaps further be supported in part by infrared spectral data. Although the far IR spectrum is not very clear, presenting strong absorptions due to hydrazine below ~ 250 cm^{-1}, no significant difference in the spectral region 250-300 cm^{-1} is observed *e.g.* between $Ni(N_2H_4)_2Cl_2$ and $Ni(N_2H_4)_3Cl_2$, thus indicating the absence of Ni–Cl stretchings around 280 cm^{-1}, as are observed in $[NiCl_4]^{2-}$ species.[22]

Conclusion

The differences observed for the spectrochemical characteristics of the axial ligands, expecially for the tetragonality parameters are conditioned by particular steric factors. This prevents us from discussing the correlations between these parameters and the chemical behaviour of the ligands in the usual manner, also owing to the already mentioned uncertainty of the tetragonality parameters. It is possible only to recognize some general tendencies; so $d\sigma$ of the halogens are distinctly negative confirming the weaker σ^*-antibonding character of the halogens with respect to nitrogen.

These values, however, are clearly influenced by the already discussed uncommon situation of the axial field; probably for this reason they do not re-

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produce the usual trend Cl>Br>I (dσ values vary very little, the apparent trend even being inverted in the two computation schemes).

Instead, in the case of *N*CS the low value of both dσ and Δ_3 confirms that the donor properties of the nitrogen of *N*CS is practically equal or only slightly smaller than that of amine nitrogen. Turning to π effects, the uncertainty of the experimental data allows us only to establish that these effects are small in absolute value, and probably not significantly different from zero for Cl and Br, while for I and *N*CS dπ is clearly positive, i.e. only for these ligands is a stronger π^*-antibonding effect than for the amine nitrogen.