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Magnetic Properties of Some Complexes of Nickel with Aromatic Diazo Compounds

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The preparation and physical properties of a number of complexes formed between divalent nickel and aromatic diazo compounds of type (substituted phenyl)-azo-2-naphthol are described. The abnormal magnetic moment of these complexes in the solid state is explained in terms of incorporation of water to give six-coordinated molecules. Experimental evidence in support of this hypothesis has been obtained by the use of X-ray, magnetic, and infrared spectroscopic methods.

Introduction

Theory shows that for an octahedral complex of nickel(II) the value of the magnetic moment is approximately 3.2 B.M. and is independent of temperature, while for a tetrahedral complex μ is a little higher and decreases with decreasing temperature.[1,2] Hence the stereochemistry of a particular compound of nickel(II) can sometimes be deduced from magnetic evidence alone.

There are a number of instances where this treatment is incomplete; for example several bis-bidentate chelates, diamagnetic in the solid state, dissolve to give paramagnetic solutions, the magnetic moment of the solute corresponding to a value intermediate between 0 and 2.8 B.M. This has been ascribed to an equilibrium between planar and either tetrahedral or octahedral configurations. Behaviour of this type has been noted in nickel complexes of amino-tropone-imines,[3,4] pyrrole-2-aldimines,[5] 2-ketoimines,[6] and in particular, N-substituted salicylaldimines[7-13] Figure 1.

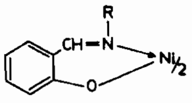

Figure 1.

Closely related to the N-arylsalicylaldimine nickel(II) complexes are the compounds formed between nickel(II) and aromatic azo-dyes of the type produced by the coupling of a diazotized aromatic amine with a phenol (Figure 2). Such a complex may be regarded as being derived from a salicylaldimine complex by replacement of the –CH=N– group by –N=N–.

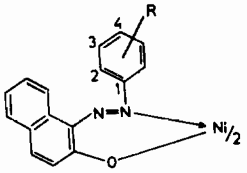

Figure 2.

Some complexes of this type were first prepared by Pfeiffer.[14] The magnetic properties of these complexes have hitherto received little attention and this paper describes the preparation and physical properties of a series of such complexes (Table I) which appear formally to be planar.

Experimental Section

U.V./Visible Spectra. Solution spectra were taken with a Cary Recording Spectrophotometer Model 14-50, and solid state reflectance spectra with a Unicam SP 500 using MgO as standard.

Magnetic Measurements were obtained using a standard Gouy balance, with cupric sulphate pentahydrate and mercuric tetrathiocyanato-cobaltate(II) standards. The values used for the gram-susceptibilities[15] are $\chi_g = 6.05 \times 10^{-6}$ and $\chi_g = 16.44 \times 10^{-6}$ cgs

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respectively. Variable temperature measurements were kindly performed by Dr. A. Earnshaw[*] with a Gouy-type balance using cupric sulphate pentahydrate as standard.

Infrared Spectra were recorded from Nujol mulls on Perkin-Elmer 257 or 521 spectrometers.

Microanalyses were performed by the microanalytical laboratory of the University Chemical Laboratory, Cambridge by the usual routine methods.

Preparation of Ligands. A series of azo-dyes was prepared by the coupling of a diazotized primary amine with 2-naphthol.[16,17] Derivatives of the following amines were prepared: aniline, p-chloroaniline, 2-naphthylamine, 2,6-xylidine, o-chloroaniline, p-bromoaniline, p-toluidine, o-toluidine, 1-naphthylamine, m-toluidine, and p-fluoroaniline. The yield in nearly all cases was 60-70% of theoretical. All of the compounds, except for a few of higher molecular weight could be recrystallized from glacial acetic acid when still wet.

In addition, several azo-dyes of para-substituted phenols were prepared by the method of Lieberman and von Kostenecki.[16] The following amines were coupled to p-cresol: aniline, 2,4-xylidine, p-fluoroaniline, and 2,4-dichloroaniline. Gentle heating was necessary in order to assist coagulation of the p-fluorophenyl derivative. Diazotized aniline was coupled to p-fluorophenol and 2,4-xylenol by Liebermann and von Kostenecki's method.

In all cases, satisfactory analyses for carbon, hydrogen and nitrogen were obtained.

Preparation of Complexes. The method of preparation of the nickel(II) complexes follows that given by Pfeiffer[14] for «o-oxyazobenzol-nickel». The compounds were purified by washing with dilute aqueous ammonia to remove excess nickel sulphate, and with ethanol to remove excess ligand. The compounds were recrystallized from mesitylene, except for some of the halogen substituted complexes.

All of the 2-naphthol dyes except 1-naphthyl-azo-2-naphthol, coordinated to nickel under the above conditions. None of the p-cresol or the other two compounds mentioned above, coordinated. A list of the complexes, with analytical results based on the formulation of the complexes as bis-chelates is given in Table I: these compounds, except the first named, are described for the first time.

Results and Discussion

U.V./Visible Spectra. The U.V./visible spectra of all complexes are very similar, and do not change greatly with change of phenyl substituent. All have bands at 313-317 mμ (extinction coefficient e = 27,000); 369-373 mμ (shoulder); 400 mμ (e = 19,000-21,000), and 580-585 mμ (e = 5000-7100). One or two slight deviations are: firstly, the band at 313 mμ for the p-fluoro compound (IX) is less intense (e = 25,000) than the rest. Secondly, the extinction coefficient of the 590 mμ band is slightly higher for the hydrocarbon substituted compounds than for the halogen substituted. Finally, the extinction coefficients of the 2-naphthyl compound (IV) are noticeably higher: 313 mμ (e = 33,000); 367 mμ (e = 33,000); 414 mμ (e = 24,000); 583 mμ (e = 8200).

These figures should be compared with those of the spectra obtained from the uncomplexed dyes: 309-320 mμ (e = 7300-7600); 320-330 mμ (shoulder); 493-487 mμ (15,700-18,300); 505-515 mμ (shoulder). Again the 2-naphthyl derivative is slightly different, the band at 306 mμ having e = 9070. The p-fluoro compound has two bands at 304 mμ (e = 6750) and 315 (shoulder) in place of the one band exhibited by the other dyes.

All the above spectra were obtained in $CHCl_3$ solution. The complexes and the ligands obeyed Beer's law. The solid-state reflectance spectra over the range 400-1000 mμ were identical with the above. It was not possible to observe the ligand field transitions as they were obscured by the far more intense charge-transfer bands just described.

Infrared Spectra. The infrared spectra of these complexes contain a large number of bands, but the majority may be assigned using Bellamy's data,[18] and that of Ueno on the o-hydroxyazobenzene complexes of Ni, Cu, and Co.[19] The spectrum of the p-bromo compound (VIII) is reproduced (Figure 3). The fol-

Table I.

	Substituent R, Figure 2	% Yield	Calculated % C	Calculated % H	Calculated % N	Calculated % Hal	Observed % C	Observed % H	Observed % N	Observed % Hal
(I)	—	92	69.49	4.01	10.13		70.12	6.55	11.4	
(II)	4—Me	90	70.03	4.48	9.65		70.93	4.58	10.0	
(III)	4—Cl	~100	61.57	3.53	9.0	11.23	62.04	3.53	9.6	11.33
(IV)	3,4-benzo	56	73.52	4.02	8.57		73.3	4.04	9.24	
(V)	2,6-dimethyl	very poor								
(VI)	2—Cl	40	61.57	3.53	9.00	11.23	62.7	3.3	9.26	11.0
(VII)	3—Me	~100	70.03	4.48	9.65		69.6	4.5	9.58	
(VIII)	4—Br	70		2.81				2.78		
(IX)	4—F	70	65.01	3.38	9.47		63.0	3.97	9.5	

(*) University of Surrey. Present address: University of Leeds.

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lowing bands (in cm^{-1}) may be assigned:

1617 m	skeletal naphthyl (see below)
1596 m 1500 m	skeletal naphthyl
1550 m	C=O of chelate ring (see below)
1378 s	N=N
1189 m 1150 s	aromatic CH deformation
820-825 s 815 s	phenyl?[18b]
737-750 s	CH of non-substituted half of nahphthyl system

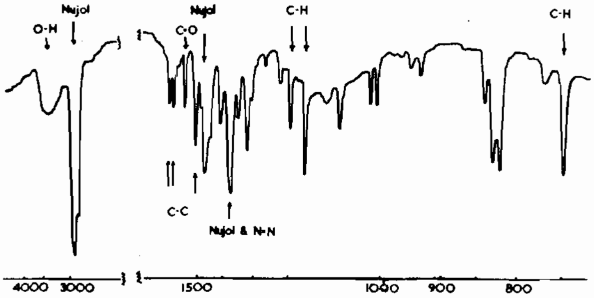

Figure 3. I.R. Spectrum of bis(p-bromophenyl-azo-β-naphtholo)nickel.

The assignment of the 1378 cm^{-1} band to the N=N system is based upon a band at 1406 cm^{-1} in free azobenzene and 1390 cm^{-1} in Ueno's complexes.[19] Bellamy[18d] quotes Le Fevre *et al.* as assigning the band at 1577 cm^{-1} in free diazo compounds to the –N=N– link, but also points out that this could be due to ring vibrations. If the band at 1545 is to be assigned to the C=O of the chelate ring, then it must be assumed that this N=N vibration completely disappears or moves to the collection of peaks below 1480 cm^{-1}, *i.e.* exhibits a shift of over 90 cm^{-1}. Either course seems a little unlikely, and the assignment of this band to the C=O in the chelate ring must be regarded as extremely tentative. This reflects the uncertainty surrounding the assignments of peaks to the –N=N– system mentioned by Bellamy.

The structure Ph–N=C– has been assigned a band in the 1639-1600 cm^{-1} region[18c] but a band in this region was not reported by Ueno. It is therefore doubtful if the band at 1617 cm^{-1} is due to the Ph–N=N– system, and it can be assigned to the naphthyl ring.[18a]

The above assignments all refer to the skeletal vibrations, and are characteristic of all of the nickel complexes under discussion, with the proviso that the doublet at 815-820 cm^{-1} sometimes collapses into one peak *e.g.* with the m-tolyl compound (VII). A broad peak at 3500-3300 cm^{-1} is apparent in the figure. This will be discussed shortly.

Magnetic Properties. None of these compounds was sufficiently soluble for measurements in solution to be carried out, even using the Evan's NMR method.[20] The magnetic moments of the complexes in the solid are:

(I)	0 B.M.	
(II)	0.0 B.M.	
(III)	1.26 B.M.	When prepared using 150 ml. acetone to dissolve the ligand, moment=0.65, 0.55 B.M.
(IV)	2.28 B.M.	
(VI)	0.62 B.M. 1	
(VII)	1.34 B.M.	Another preparation gave 1.59 B.M.
(VIII)	3.44 B.M.	
(IX)	1.59 B.M.	

The low values obtained, less than the «spin only» value for two upaired electrons, call for an explanation. The susceptibility and moment of a sample of bis(p-fluorophenyl-azo-2-naphtholo)nickel-(II) (compound IX) is shown as a function of temperature in Figure 4. The moment is constant at 1.69 B.M., and the susceptibility shows a straight line dependence. A sample of the m-tolyl complex (VII) also showed a straight line dependence with moment=0.50 B.M.

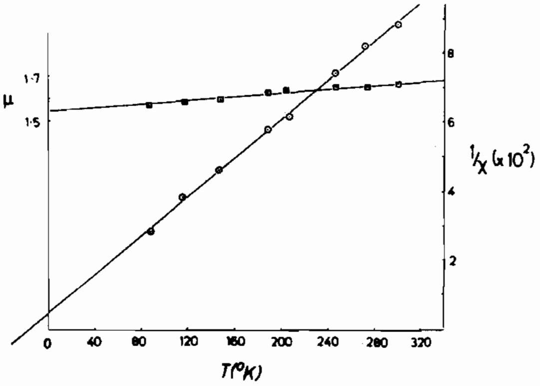

Figure 4.

The following hypotheses could account for the unusual magnetic properties of these complexes:

(1) Nickel atoms occupy planar and tetrahedral coordination positions, or planar and octahedral coordination positions. This could be achieved in two ways: (a) the compounds crystallize in two distinct forms, one crystal form containing the diamagnetic planar environments, the other form containing the paramagnetic, (b) the two environments are found together in the same crystal. Octahedral and planar forms of the same compound in the same crystal have been shown to exist in the case of bis(meso-stilbenediamine)nickel) dichloroacetate,[21] and a mixture of tetrahedral and planar forms in the same crystal occurs in bis(benzyldiphenyl-phosphine)dibromonickel.[22] The magnetic moment of a mixture containing tetrahedral molecules would be expected to decrease with decreasing temperature, in the manner described above, the moment of a mixture containing octahedral molecules would be independent of temperature. The

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experimental results obtained are therefore in accordance with a mixture of planar and octahedral forms.

(2) A Boltzman distribution between a singlet ground state and excited triplet state would give an effective magnetic moment intermediate between 0 and 2.8 B.M. A Boltzman distribution of this type would lead to the expression:

$$\chi_M = \frac{2g^2N\gamma^2}{3kT} \cdot \frac{1}{1+1/3\,.\exp\,(J/kT)}$$

where γ is the Bohr magneton, g is the Landé splitting factor, and J is the energy difference between the two levels[23,24] (the so-called «exchange integral»). A relationship of this sort would not give a straight line dependence of χ^{-1} on T unless $J=0$. A Boltzman distribution of this type could be achieved in three ways:

(a) The energy separation between the two highest orbitals in a square-planar complex is comparable to the pairing energy.

(b) The energy difference between the two highest d-orbitals in an octahedral complex suffering tetragonal distorsion is comparable to the pairing energy. Behaviour of this type has been reported for Fe(o-phenanthroline)$_2$(NCX)$_2$ (X=S or Se).[25,26] Several nitrosyl adducts of iron compounds are reported to show this behaviour,[27,28] whilst the theoretical aspects have been discussed.[29,31] Several complexes of divalent nickel with large organic ligands have also been shown to behave similarly.[32,33,34]

(c) Distortion of the complex such that it could be regarded as being intermediate between a planar and tetrahedral molecule would reduce the energy difference between the $d_{x^2-y^2}$ and d_{xy} orbitals (Figure 5).

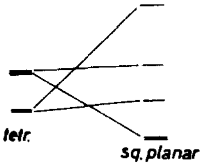

Figure 5.

Distortions of this nature have been observed for some copper-salicylaldimine complexes[35,36] but distortions for nickel chelates from strictly planar or tetrahedral symmetries are smaller.[37,38]

(3) So far, only «magnetically dilute» systems have been considered. If antiparallel alignment of spins exists between the nickel atoms throughout the whole of the crystal we have an intermolecular antiferromagnetic system. Such systems are characterised by a steadily increasing susceptibility with increasing temperature, until the Néel temperature is reached, after which the fall characteristic of normal paramagnetic compounds is observed. This form of temperature dependence has not been shown by the complexes under investigation. Examples of nickel compounds exhibiting antiferromagnetism, such as NiO, NiS, KNiF$_3$, illustrate that the paramagnetic centres must be in close proximity for interaction to occur.

(4) Intermediate between the magnetically «dilute» paramagnetic and magnetically «concentrated» intermolecular antiferromagnetic systems may be recognised the «intramolecular antiferromagnetic» case, in which spin exchange takes place between a small number of centres. There are a large number of examples of complexes showing this behaviour, mostly binuclear complexes of copper, although cobalt, chromium and ferric iron also show this exchange.[39-45] Very few examples are known for nickel, but one interesting compound is Ni$_2$Br$_3$en$_4$(ClO$_4$)$_3$ (en = ethylenediamine) which has a magnetic moment of 1.17 B.M. per Ni atom, but which formally contains Ni^{3+}.[46]

Two interacting Ni^{2+} atoms, each with $S=1$ will generate three possible states characterised by $S=0$, 1 or 2, depending upon the relative alignment of the atomic moments. A Boltzman distribution over these levels would lead to the expression:

$$\chi_M = \frac{Ng^2\gamma^2}{3kT} \cdot \frac{3\,.\exp(4x)+15}{\exp(6x)+3\,.\exp(4x)+5} \qquad (x=J/kT)$$

where J is again the «exchange integral». This expression will not give a straight line dependence of $1/\chi$ with T and a plot of the above function will have the same shape qualitatively as the antiferromagnetic compounds discussed in (3) above. This cannot be an explanation for the magnetic properties of the azo-dye complexes.

The following is advanced to account for the experimental observations.

The compounds consist of a mixture of planar and octahedral molecules. On the basis of a single-crystal X-ray study of the m-tolyl compound (VII) to

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be reported, the possibility was eliminated of the side-by-side existence of two types of crystal, one containing planar, the other octahedral molecules. The unit cell constants, as derived from a bulk powder pattern were the same as those derived from single-crystal photographs. Hence the two environments must exist side-by-side in the same crystal.

Intermolecular association, similar to that proposed for bis(N-methylsalicylaldimine)nickel[47,48] was not found possible, the shortest intermolecular Ni...O distance being 3.89 Å.

The octahedral molecules could be formed from the planar ones by the coordination above and below the plane of two molecules of water. The quantity of absorbed water would probably be dependent on the steric effects of the ligands—some ligands producing a more open structure with more «holes» suitable for incorporation of the water. This is a possible explanation of the variation in magnetic moment with different substituents noted earlier.

The most characteristic band due to the H_2O group is the broad O–H stretching frequency at approximately 3500 cm^{-1}. The I.R. spectra of the p–CH_3, p–F, and p–Br complexes (II, IX, and VIII) over the range 4000-2500 cm^{-1} are reproduced Figure 6.

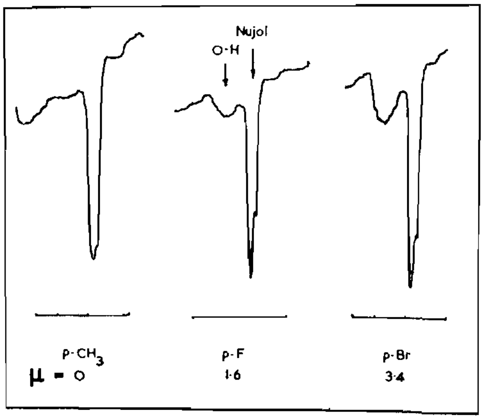

Figure 6. I.R. Spectra over the range 4000-2500 cm^{-1}.

The magnetic moments of these complexes are 0, 1.59, and 3.44 B.M. respectively, and it can be seen that this increase is paralleled by an increase in the intensity of a broad band centred at 3400 cm^{-1}. The noise-level in the p–CH_3 spectrum is rather high, but the absence of a peak here, and the significant peak emerging with the p–Br compound is obvious.

Taking the p-fluoro compound (IX) as a typical example, and assuming that 100% incorporation of water corresponds to a magnetic moment of 3.4 B.M., the values of 1.6 B.M. for IX then corresponds to $(1.6/3.4)^2$ *i.e.* 25% incorporation. The «effective molecular weight» now becomes $(588.7+1/4.36)=$ 597.7 and the new theoretical analysis figures are C=64.2%, H=3.51%, N=9.37%, as compared with the earlier figures of 65.01, 3.38, and 9.47% respectively. The detection, by means of analysis, of this water is outside the limit of experimental error.

The results of the X-ray study of the m-tolyl compound (VII) are presented in full elsewhere, but as the results fully confirm the above hypothesis, a brief summary is given here. Bis(m-tolyl-azo-2-naphtholo)-nickel is monoclinic, with

a	=	16.532 Å	e.s.d. = 0.0059 Å
b	=	5.082	0.0007
c	=	19.382	0.0081
beta	=	125.041°	0.025°
volume	=	1333.17 $(Å)^3$	0.63 $(Å)^3$

Calculated density for two molecules per unit cell= 1.448 gm/cc. observed density=1.40 gm/cc. Space group=$P2_1/c$. In this space group, only two molecules per unit cell means either that the molecules must lie on a crystallographic centre of symmetry, or, less probably, the structure is completely random. The refinement of the structure to an R factor of 12.7% indicates that the former is correct, and that the structure consists of essentially square-planar molecules with the possibility existing for raising the coordination number to six, by the incorporation of water in the manner just described.

Brubaker and Busch[49] have investigated the properties of the complex dibromo-S,S′-o-xylyl-2,3-pentanedionebis(mercaptoethylimine)nickel, which exists in two forms, one green, the other red-brown. The green form is paramagnetic, and is produced when the compound is handled in a dry-box. When exposed to the air, the brown form is produced, 0.5 moles of water are absorbed, and the magnetic moment is reduced to 1.2 B.M. The X-ray powder patterns of the two forms reveal no changes in the crystal spacings, though some of the intensities are diminished in the powder pattern of the brown form. This suggests that the wetting of the crystal to destroy the paramagnetism occurs without greatly altering the crystal structure. Similarly it is reasonable in the azo-dye complexes here to propose that the absorption of water does not affect the crystal structure. This would account for the ability of *e.g.* the p-chloro complex (III) to exhibit different magnetic moments depending upon the history of the sample. When a sample of the m-tolyl compound (VII) was recrystallized slowly from mesitylene for the X-ray study, the moment decreased from 1.34 to 0.5 B.M., again compatible with the above hypothesis.

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