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Aromatic Diamine Complexes. I. Nickel(II) Complexes with o-Phenylenediamine, 1,8-Diaminonaphthalene and 2-2-Diaminobiphenyl

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Nickel(II) complexes containing two and three molecules of the aromatic diamines, o-phenylenediamine, 1,8-diaminonaphthalene and 2-2'-diaminobiphenyl are described. The complexes have been characterised by magnetic and infrared and visible spectral, measurements. Those complexes containing two molecules of diamine have been shown to have D_{4h} symmetry. The significance of the tetragonal splitting parameter Dt and axial ligand field strengths Dq^z of the acid groups is discussed.

Introduction

Complexes formed by various aliphatic diamines and transition metal ions have been intensively studied for many years. Although there have been scattered reports of complexes with aromatic diamines[1-13] a thorough study of these complexes has not been carried out

This investigation was commenced to characterise and deduce the structures of complexes with the aromatic diamines, o-phenylenediamine, 1,8-diaminonaphthalene and 2-2'-diaminobiphenyl. Recently, two papers concerning complexes of o-phenylenediamine have been published.[14-15] It appears that the complexes obtained with this ligand are strongly influenced by the conditions under which the preparations are carried out.

Nickel(II) complexes containing two and three molecules of aromatic diamine are reported here, their structures having been deduced by infrared and visible spectroscopy, and magnetic properties.

Experimental Section

Materials. o-Phenylenedamine (opda), (Eastman Kodak), was recrystallised from ethanol containing decolourising charcoal. 1,8-Diaminonaphthalene (dan), (Koch-Light Practical Grade), was recrystallised from 100-120° petroleum ether. 2-2'-Diaminobiphenyl (dabp), was prepared bythe reduction of 2-2' dinitrobiphenyl (BDH), with stannous chloride in hydrochloric acid.[16] The crude product obtained was recrystallised from a 1:1 mixture of benzene and 80-100° petroleum ether. Nickel perchlorate was prepared from nickel carbonate and perchloric acid, and recrystallised from ethanol. Nickel thiocyanate and nickel iodide were prepared *in situ* by the reaction of nickel nitrate hexahydrate in ethanol with potassium thiocyanate or potassium iodide respectively. The precipitated potassium nitrate was removed by filtration, and the ethanolic filtrate used for the preparation of complexes.

Preparation of Nickel Complexes. A warm ethanolic solution of the hydrated nickel salt (0.001 mole in [illegible] solution of the diamine. The ratios of nickel ion to diamine used are given in Table I. The complexes precipitate immediately or crystallise out on cooling overnight. The solid complexes were removed by filtration, washed with ethanol and dried under vacuum.

Infrared Spectra. Infrared absorption spectra in the range 4000-400 cm^{-1} were obtained using a Perkin Elmer model 125 recording spectrophotometer. Nujol and hexachlorobutadiene mull techniques were used. Far infrared spectra (400-40 cm^{-1}) were obtained on samples dispersed in polyethylene on an R.I.I.C., F.S. 620 interferometer, and computed on an F.T.C. 100 computor to a limiting resolution of 2.5 cm^{-1}. The spectra were calibrated against water vapour.

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Table I.

Compound	Ratio Ni : Ligand Used	Calculated %			Found %		
		C	H	N	C	H	N
$Ni(opda)_2Cl_2$	1 : 3	41.86	4.65	16.27	41.80	4.78	16.30
$Ni(opda)_2Br_2$	1 : 1	33.10	3.67	12.87	33.05	3.85	13.05
$Ni(opda)_3Br_2$	1 : 3	39.85	4.43	15.50	39.54	4.62	15.39
$Ni(opda)_2I_2$	1 : 1	27.22	3.02	10.58	26.92	3.21	10.81
$Ni(opda)_3I_2$	1 : 3	33.92	3.90	13.21	33.64	4.15	13.03
$Ni(opda)_2(NO_3)_2$	1 : 3	36.17	4.62	21.11	35.97	4.59	20.86
$Ni(opda)_3(ClO_4)_2$	1 : 3	37.23	4.13	14.48	37.20	4.24	14.51
$Ni(opda)_2(NCS)_2$	1 : 3	42.96	4.09	21.48	42.87	4.29	21.06
$Ni(dan)_2Cl_2$	1 : 3	54.05	4.50	12.58	54.38	5.10	12.29
$Ni(dan)_2Br_2$	1 : 2	44.85	3.73	10.46	44.98	4.04	10.36
$Ni(dan)_3Br_2$	1 : 3	52.03	4.33	12.13	51.86	4.26	12.37
$Ni(dan)_2I_2$	1 : 2	38.15	3.17	8.90	38.49	3.36	8.92
$Ni(dan)_3I_2$	1 : 3	45.80	3.81	10.68	45.74	3.83	10.59
$Ni(dan)_2(NO_3)_2$	1 : 3	48.19	4.02	16.86	48.37	4.29	16.35
$Ni(dan)_3(ClO_4)_2$	1 : 3	49.24	4.10	11.49	48.64	4.65	10.88
$Ni(dan)_2(NCS)_2$	1 : 3	53.76	4.07	17.10	53.85	4.39	16.46
$Ni(dabp)_2Cl_2$	1 : 3	57.83	4.81	11.26	57.32	5.41	10.70
$Ni(dabp)_2Br_2$	1 : 3	49.06	4.08	9.54	49.53	4.79	9.59
$Ni(dabp)_2I_2$	1 : 3	42.29	3.52	8.22	42.39	3.77	8.66
$Ni(dabp)_2(NO_3)_2 . H_2O$	1 : 3	50.60	4.57	14.78	50.12	4.86	13.73
$Ni(dabp)_3(ClO_4)_2 . 2H_2O$	1 : 3	51.15	4.73	9.92	51.82	5.27	9.17
$Ni(dabp)_2(NCS)_2$	1 : 3	57.45	4.41	15.46	57.36	4.58	14.74

Reflectance Spectra. Reflectance spectra were obtained over the range 6000-28000 cm^{-1} using a Perkin Elmer model 450 recording spectrophotometer. The samples were mounted on filter paper.

Magnetic Measurements. Magnetic measurements were made by the Gouy method, using $Hg[Co(NCS)_4]$ as calibrant. Susceptibilities of ligands and anions were calculated from Pascal's constants [17]

Analyses. Analyses for carbon, hydrogen and nitrogen were performed by A. Bernhardt, Microanalytical Laboratories, W. Germany. Nickel was estimated by precipitation with dimethylglyoxime.

Results and Discussion

The complexes obtained with the three aromatic diamines, o-phenylenediamine (opda), 1,8-diaminonaphthalene (dan), and 2-2′-diaminobiphenyl (dabp), are reported in Table I, together with the ratios of nickel ion to ligand used in their formation and analytical data. Table II records the infrared spectra in the region 4000-400 cm^{-1} for the ligands and the bis-diamine chloride complexes. The spectra of the ligands are very similar in all derivatives with any one diamine, and the chlorides are quoted as representative. Coordination of the diamine to the nickel ion results in a lowering of the position of the N–H stretching, NH_2 deformation, and C–N stretching, frequencies. Thus in the bis and tris complexes reported, it is concluded that all three diamines are behaving as bidentate ligands. The same conclusion was reached by Marks *et al.*[14] for bis and tris o-phenylenediamine complexes. The thiocyanate complexes show absorptions assigned to $\nu(C{\equiv}N)$ at 2100 cm^{-1}; $\nu(C–S)$ at 800 cm^{-1} and $\delta(N–C–S)$ between 470 and 480 cm^{-1}. These absorptions indicate that thiocyanate is bonded through the nitrogen atom to the nickel ion.[18] The nitrate complexes with o-phenylenediamine and diaminonaphthalene show strong bands at 1410 cm^{-1}, 1310-1320 cm^{-1} and 1030-1040 cm^{-1}. With diaminobiphenyl, only bands at 1410 and 1330 cm^{-1} were observed, a strong ligand absorption obscuring any band in the 1040 cm^{-1} region. These features indicate that the nitrate anion is coordinated to the nickel in all three complexes.[19] The latter complex also has an abosorption at 3520 cm^{-1} associated with the presence of water (see Table I). The perchlorates all exhibit strong, broad absorptions in the 1140-1000 cm^{-1} region, indicating uncoordinated perchlorate.[20] The diaminobiphenyl complex also has an absorption at 3520 cm^{-1} due to the presence of water (Table I).

The room temperature magnetic properties of the complexes are shown in Table III. All complexes have magnetic moments in the range 3.0 to 3.3 Bohr Magnetons, indicating a triplet ground state, and an octahedral or distorted octahedral environment about the nickel ion.

The solid reflectance spectra of the complexes containing three molecules of diamine per nickel ion are shown in Table IV. For any one diamine, the spectra of the complexes are very similar, the anions being assumed to be ionic and the nickel ion to be surrounded by six nitrogen donor atoms from the three diamine molecules. The spectra are characteristic of the nickel(II) ion with a triplet ground state in an octahedral environment, (true symmetry D_3). The absorption bands may be assigned in O_h symmetry as: ν_1, $^3A_{2g}\rightarrow{}^3T_{2g}$; ν_2, $^3A_{2g}\rightarrow{}^3T_{1g}$; ν_3, $^3A_{2g}\rightarrow{}^3T_{1g}(P)$. The position of the first absorption band for nickel(II) in

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Table II. Infrared Data (4000-400 cm^{-1})

opda	Ni(opda)$_2$Cl$_2$	dan	Ni(dan)$_2$Cl$_2$	dabp	Ni(dabp)$_2$Cl$_2$	
3380 s	3290 s	3410 s	3240 s	3400 s	3300 s	
3360 s	3195 s	3380 s	3170 s	3380 s	3220 s	N–H st.
3280 s	3150 s	3330 s	3120 s	3270 s	3140 s	
3180 s	3110 s	3300 s		3170 s		
3020 m	3020 m	3020 m	3020 sh	3050 s	3020 s	C–H st.
1620 m	1600 m	1610 m	1605 m	1630 s	1610 s	NH$_2$ def.
1585 m	1570 m	1578 m	1578 m	1600 m	1590 m	C$_6$ ring
				1585 m	1575 m	
1475 m	1490 s	1400 m	1400 m	1480 s	1485 s	C$_6$ ring
		1355 m		1315 m	1290 m	
		1300 s	1275 m	1300 m	1275 m	
1270 s						C–N st.
1240 m	1245 m			1250 m	1230 m	
1150 m	1212 m	1150 m	1120 m	1150 m	1160 m	
1050 w	1095 m	1070 m	1085 sh	1040 m	1070 m	
1025 w	1030 sh	1020 m	1070 m	1000 m	1040 s	
	1015 s		990 m	935 m	1000 m	
920 m	940 w			928 m	935 m	
865 sh		810 s	810 m	860 m	865 m	
850 sh		770 m	750 m	750 m	830 m	
740 s	750 s	750 s	720 w	725 s	755 s	
720 sh					730 m	
	620 m	635 m	625 m		640 m	
			615 m			
				570 m	570 m	
				560 m		
530 w	560 m	520 w		525 m		
460 m		480 m	485 w	480 m	495 m	
450 m	450 m	465 m				
435 m						

Table III. Room temperature magnetic properties

Compound	Temp °K	$\chi_m^{corr} \times 10^6$	μ_{eff} B.M.^{a}
Ni(opda)$_2$Cl$_2$	293	4313	3.18
Ni(opda)$_2$Br$_2$	294	4026	3.10
Ni(opda)$_3$Br$_2$	293	4109	3.12
Ni(opda)$_2$I$_2$	294	3917	3.05
Ni(opda)$_3$I$_2$	292	4207	3.14
Ni(opda)$_2$(NO$_3$)$_2$	293	4364	3.20
Ni(opda)$_3$(ClO$_4$)$_2$	295	4106	3.12
Ni(opda)$_2$(NCS)$_2$	296	4801	3.32
Ni(dan)$_2$Cl$_2$	294	3763	3.02
Ni(dan)$_2$Br$_2$	292	4324	3.18
Ni(dan)$_2$I$_2$	294	3799	3.02
Ni(dan)$_3$Br$_2$	294	4350	3.20
Ni(dan)$_3$I$_2$	295	3941	3.08
Ni(dan)$_2$(NO$_3$)$_2$	293	3923	3.05
Ni(dan)$_3$(ClO$_4$)$_2$	295	3999	3.08
Ni(dan)$_2$(NCS)$_2$	294	3973	3.07
Ni(dabp)$_2$Cl$_2$	294	4543	3.26
Ni(dabp)$_2$Br$_2$	295	4219	3.17
Ni(dabp)$_2$I$_2$	295	3854	3.02
Ni(dabp)$_2$(NO$_3$)$_2$. H$_2$O	295	4023	3.10
Ni(dabp)$_3$(ClO$_4$)$_2$. 2H$_2$O	294	4275	3.18
Ni(dabp)$_2$(NCS)$_2$	296	3948	3.07

^{a} Calculated from $\mu_{eff} = 2.84\sqrt{\chi_m^{corr} \times T°K}$.

Table IV. Reflectance Spectra of the tris complexes

Compound	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}
Ni(opda)$_3$Br$_2$	10600	17500	>28000
Ni(opda)$_3$I$_2$	10600	17500	>28000
Ni(opda)$_3$(ClO$_4$)$_2$	10700	17700	>28000
Ni(dan)$_3$Br$_2$	11100	~21000 (br)	>28000
Ni(dan)$_3$I$_2$	11120	~21000 (br)	>28000
Ni(dan)$_3$(ClO$_4$)$_2$	11200	~20000 (br)	>28000
Ni(dabp)$_3$(ClO$_4$)$_2$. 2H$_2$O	10500	16700	~25000 (br)

O_h symmetry allows a value for the octahedral ligand field strength (10Dq) for each diamine to be obtained. Thus for o-phenylenediamine, 10Dq = 10650 cm^{-1}; diaminonaphthalene, 10Dq = 11150 cm^{-1} and diaminobiphenyl, 10Dq = 10500 cm^{-1}. A "spectrochemical series" for the diamines is thus dabp < opda < dan. The strongest ligand field is produced by diaminonaphthalene which forms a six membered chelate ring with the nickel ion, the next strongest o-phenylenediamine (five membered) and the weakest diaminobiphenyl (seven membered). Models indicate that considerable strain is produced in the chelate ring when o-phenylenediamine and diaminobiphenyl are attached in *cis* positions to the octahedral nickel ion, but diaminonaphthalene may be attached with very little resultant strain in the chelate ring. Both o-phenylenediamine and diaminonaphthalene give rise to smaller ligand field splittings than the corresponding aliphatic diamines, ethylenediamine and 1,3 propanediamine.[21]

For the complexes containing two molecules of diamine per nickel ion, Ni(diamine)$_2$X$_2$, two stereochemical arrangements are possible, *cis* (C_{2v}) or *trans* (D_{4h}). Two complementary techniques have been used to elucidate the structure of these complexes.

If we consider the Ni–X vibrations, for a molecule of the type *cis* NiN$_4$X$_2$ (C_{2v}), (N = donor atom), two infrared active Ni–X stretching vibrations should be observed, whereas for *trans* NiN$_4$X$_2$ (D_{4h}), we expect

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only one.[22,23] Infrared spectra in the 400-40 cm^{-1} region are recorded in Table V. Halogen sensitive absorption bands have been assigned as ν(M–X) and δ(M–X). For the Ni(diamine)$_2$X$_2$ complexes, only one ν(M–X) vibration is detected, suggesting that these compounds have the *trans* (D_{4h}) configuration. For the diaminonaphthalene halide complexes, the positions of ν(M–X) for chloride, bromide and iodide are considerably lower than those for the corresponding halide complex with o-phenylenediamine and diaminobiphenyl. It has been suggested that the splitting of the ν(M–X) band in thiourea complexes, *trans* Nitu$_4$X$_2$, is associated with the unequal Ni–X bond distances for the two *trans* halides.[24] Thus it appears that the diaminonaphthalene complexes are considerably more tetragonally distorted, with possibly longer Ni–X bond distances than the complexes with the other two ligands. The positions of ν(M–N) for all the complexes and ν(M–X) and δ(M–X) where appropriate, are of the order of 10 cm^{-1} higher than the corresponding cobalt(II) complexes[25] as expected from the Irving-Williams order of stabilities.

Table V. Infrared Spectra. 400-40 cm^{-1}

Compound	ν(M–X) cm^{-1}	δ(M–X) cm^{-1}	ν(M–N) cm^{-1}
Ni(opda)$_2$Cl$_2$	220	112	272
Ni(opda)$_2$Br$_2$	135	102	266
Ni(opda)$_3$Br$_2$	—	—	286
Ni(opda)$_2$I$_2$	120	80	262
Ni(opda)$_3$I$_2$	—	—	286
Ni(opda)$_2$(NO$_3$)$_2$	180	—	284
Ni(opda)$_3$(ClO$_4$)$_2$	—	—	286
Ni(opda)$_2$(NCS)$_2$	184	—	272
Ni(dan)$_2$Cl$_2$	144	92	300 [a]
Ni(dan)$_2$Br$_2$	112	66	300 [a]
Ni(dan)$_3$Br$_2$	—	—	290 [a]
Ni(dan)$_2$I$_2$	80	52	290 [a]
Ni(dan)$_3$I$_2$	—	—	290 [a]
Ni(dan)$_2$(NO$_3$)$_2$	130?	—	290 [a]
Ni(dan)$_3$(ClO$_4$)$_2$	—	—	290 [a]
Ni(dan)$_2$(NCS)$_2$	196?	—	280 [a]
Ni(dabp)$_2$Cl$_2$	232	116	300 [a]
Ni(dabp)$_2$Br$_2$	144	100	300 [a]
Ni(dabp)$_2$I$_2$	124	86	292 [a]
Ni(dabp)$_2$(NO$_3$)$_2$. H$_2$O	160?	—	284 [a]
Ni(dabp)(ClO$_4$)$_2$. 2H$_2$O	—	—	272
Ni(dabp)$_2$(NCS)$_2$	224	—	270

[a] Shoulder on ligand absorption. ν=Stretching mode. δ= Bending mode.

The electronic spectra of nickel(II) compounds of D_{4h} symmetry and a triplet ground state have recently been discussed.[26,27,28] The $^3T_{2g}$ and $^3T_{1g}$(F) levels in O_h symmetry are split in D_{4h} symmetry into $^3B_{2g}$ and ^3E_g and $^3A_{2g}$ and ^3E_g respectively. Thus for the nickel(II) ion in D_{4h} symmetry, we expect four absorption bands in the region 7000-18000 cm^{-1}, whereas only two should be observed if the symmetry is O_h. Figure 1 records the reflectance spectra in this region for Ni(dabp)$_3$(ClO$_4$)$_2$, (O_h symmetry) and Ni(dabp)$_2$Br$_2$ (D_{4h} symmetry). The reflectance spectra of the bis-diamine complexes are listed in Table VI. The position of ν_5 is not quoted with great accuracy due to the presence of charge transfer bands in this region. The general features of all the spectra are similar, and assignment of the transitions in D_{4h} symmetry is justified. Thus ν_1: $^3B_{1g} \rightarrow {}^3E_g$; ν_2: $^3B_{1g} \rightarrow {}^3B_{2g}$; ν_3: $^3B_{1g} \rightarrow {}^3A_{2g}$; ν_4: $^3B_{1g} \rightarrow {}^3E_g$. The transition ν_1 is related to the tetragonal distortion of the complexes, whereas ν_2 should be independent of the parameters Ds and Dt,[29] if the off diagonal terms of the tetragonal distortion are neglected, and a measure of the in plane ligand field Dq^{xy}. Thus the position of ν_2 should be independent of the axially coordinated anion in the bis-diamine complexes and similar to that of ν_1 for the corresponding tris-diamine complexes with O_h symmetry. Comparison of ν_2(D_{4h}) with ν_1(O_h) for one diamine (see Table IV) shows that this is the case, there being only small variations in position.

Table VI. Reflectance Spectra and crystal field parameters of the bis complexes

Compound	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}	ν_5, cm^{-1}	Dt, cm^{-1}	Dq^z, cm^{-1}
Ni(opda)$_2$Cl$_2$	8650	?	12750	17550	27200	228	665
Ni(opda)$_2$Br$_2$	8000	10700 w	13400 sh	17000	26600	303	535
Ni(opda)$_2$I$_2$	7900	10800 w	13500	17000	26800	314	515
Ni(opda)$_2$(NO$_3$)$_2$	9200	10700 w	13500	18350	>28000	166	775
Ni(opda)$_2$(NCS)$_2$	~11800	10700 sh	13500	18200	>28000	–131	1295
Ni(dan)$_2$Cl$_2$	7700	11000	15200	~19000	~24000 br	394	425
Ni(dan)$_2$Br$_2$	7600	11000	15600	~20000	~24000 br	405	405
Ni(dan)$_2$I$_2$	7250	11000	15200 sh	~21000	>28000	445	335
Ni(dan)$_2$(NO$_3$)$_2$	7800	11100	15200 sh	~21000	>28000	383	445
Ni(dan)$_2$(NCS)$_2$	12200	11000	?	~20000	>28000	–120	1335
Ni(dabp)$_2$Cl$_2$	8500	10300	~14000 sh	16100	24300	228	650
Ni(dabp)$_2$Br$_2$	7750	10500	13800 sh	15700	24300	314	500
Ni(dabp)$_2$I$_2$	7500	10600	13800 sh	15600	[a]	335	450
Ni(dabp)$_2$(NO$_3$)$_2$. H$_2$O	7700	10500	13800 sh	16400	24800 sh	320	490
Ni(dabp)$_2$(NCS)$_2$	11800	10600	?	17100	[a]	–149	1310

[a] Charge transfer band obscures ν_5.

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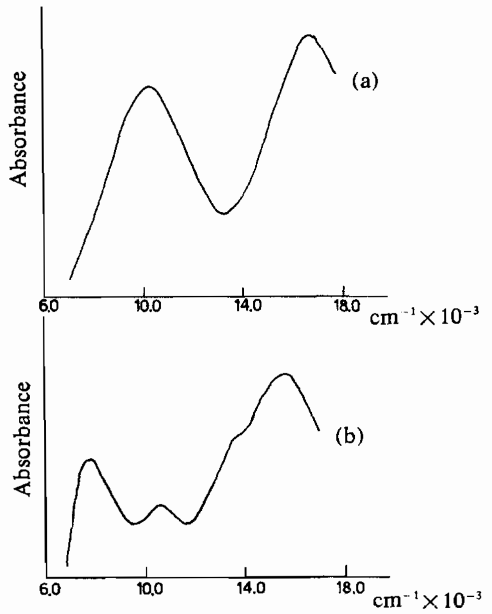

Figure 1. Reflectance Spectra: (a) $Ni(dabp)_3(ClO_4)_2$; (b) $Ni(dabp)_2Br_2$.

For the calculation of Dt, the value of Dq^{xy} was taken from the average position of $\nu_1(O_h)$, *i.e.* Dq^{xy} (opda) = 1065 cm^{-1}, Dq^{xy} (dan) = 1115 cm^{-1}, Dq^{xy} (dabp) = 1050 cm^{-1}. The sign of Dt should give an indication which of the states ^3E_g and $^3B_{2g}$ arising from $^3T_{2g}$ in O_h symmetry lies lowest.[26] If Dq^z (the axial ligand field strength) is less than Dq^{xy}, then Dt will be positive, the octahedron will be elongated along the z axis and ^3E_g will lie below $^3B_{2g}$. If Dq^z is greater than Dq^{xy}, Dt will be negative and $^3B_{2g}$ will lie below ^3E_g. In this case, ν_1 will arise at higher energy than ν_2.

Values of Dt and Dq^z for the bis-diamine complexes were calculated and are recorded in Table VI. In all cases excepting for the thiocyanate derivatives, the value of Dt is positive suggesting elongation along the z axis, with Dq^z being weaker than Dq^{xy}. For the thiocyanates, Dt is negative and Dq^z is greater than Dq^{xy}.

For the o-phenylenediamine and diaminonaphthalene complexes, the spectrochemical series is thus:

$$I^- < Br^- < Cl^- < NO_3^- < \text{diamine} < NCS^-$$

However for the diaminobiphenyl complexes:

$$I^- < NO_3^- \sim Br^- < Cl^- < \text{dabp} < NCS^-.$$

The "anomalous" position of the nitrate ion in the series of diaminobiphenyl complexes is probably associated with the presence of the water molecule in the nitrate derivative. If the water molecule is hydrogen bonded to two nitrate ions along the z axis in a bridging manner, this could reduce the metal-oxygen bond strength with the result that the ligand field strength of the nitrate in the axial positions becomes comparable to that of the bromide ion. The nitrate would thus have a polymeric structure held together by the bridging water molecules.

If the values of Dt and Dq^z for the halide complexes with the three ligands are compared, and it should be remembered that these are approximate values due to the treatment employed which has neglected off diagonal terms, those for a particular halide are similar for o-phenylenediamine and diaminobiphenyl, but considerably different to the values for diaminonaphthalene. The values indicate much larger tetragonal distortions for the diaminonaphthalene complexes, and much lower values of Dq^z for the halide ions.

Earlier in this paper, the positions of ν(M–X) for the diaminonaphthalene halide complexes were found to be considerably lower than those for the corresponding o-phenylenediamine and diaminobiphenyl complexes. This suggested that the complexes with diaminonaphthalene were more tetragonally distorted than the other two ligands, and had longer M–X bond distances.

Thus the values of Dq^z and ν(M–X) both indicate strong tetragonal distortion and weak axial bonding for the diaminonaphthalene complexes. The correlation between these two factors has not been noted previously, and the generality of its application is being further investigated with other ligands.

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