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The Spectra and Structure of Transition Metal Complexes with Tetradentate Macrocyclic Ligands

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A systematic account is given of data on the structures and spectroscopic properties of transition metal complexes with synthetic tetradentate macrocyclic ligands. The principal types of the structures of such complexes are specified. On the basis of the analysis of electronic absorption spectra, a conclusion is reached concerning the mutual influence of the ligands, which is expressed by a consistent variation of the spectrochemical parameters.
The bibliography includes 191 references.

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I. INTRODUCTION

Macroheterocyclic compounds represent the structural elements of many important natural metal complexes such as haem, vitamin B_{12}, chlorophyll, and others. The chemistry of these compounds has now been thoroughly investigated[1] and many complexes of porphyrins and corrins have been synthesised *in vitro*[2,3]. Only high-intensity bands, associated with intraligand transitions and (or) charge-transfer bands, which mask the $d-d$ transition bands, have been observed in the electronic spectra of compounds of this type. The problems of the spectroscopy of porphyrin complexes have been described in detail in a monograph[4].

The chemistry of synthetic ligands, i.e. ligands which are not encountered in living nature and which constitute models of natural macrocycles, has developed vigorously during the last decade. There have been a number of reviews devoted to various aspects of the chemistry of metal complexes with ligands of this type[5-8], but the problems of the spectroscopy of these compounds have been considered only briefly in Busch's review[5] published in 1967.

This review deals with the crystal structures and electronic absorption spectra of complexes formed by metal ions having unfilled d shells with synthetic tetradentate macrocyclic ligands containing either donor atoms of one kind (nitrogen or sulphur) or donor atoms of different kinds (nitrogen, sulphur, and oxygen). The compounds under consideration include also complexes with ligands having a large number of donor atoms, among which only four are involved in coordination. Attention is concentrated on the absorption spectra associated with the excitation of the d electrons of the metal ions, which precludes the inclusion of porphyrin and corrin complexes in this review. The review covers the literature up to 1977 inclusive.

The ligands are designated using the namenclature proposed by Busch and coworkers[9,10], which we believe to be most suitable, despite some ambiguity.

Macrocyclic ligands, whose complexes are considered in this review, and their names are given in Fig.1. Other most frequently encountered names of individual ligands are given in brackets.

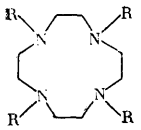
II. THE STRUCTURE OF COMPLEXES WITH MACROCYCLIC LIGANDS

In the majority of the complexes dealt with in this review the donor atoms of the macrocyclic ligand occupy the equatorial plane in the coordination sphere of the metal. This type of coordination enables the ligand to assume the most convenient conformation to which corresponds the minimum strain in the macroring. However, in such coordination another source of strain in the macroring is generated. The maximum overlap of the metal orbitals with the occupied donor orbitals of the ligand is observed when the latter are directed along the diagonals of the tetragon formed by the donor atoms. In the ligands considered below the size of the macroring prevents the ligands from assuming such a conformation and the incorporation of the metal ion in the plane of the donor atoms therefore leads to the occurrence of strain in the donor atom–carbon atom bonds.

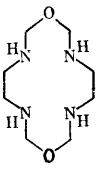
The "ideal" metal–donor atom distances have been calculated as a function of the size of the macroring[11] by the ligand strain minimisation method. It follows from the results that a 14-membered macrocyclic ligand will experience the minimum strain on coordination to the cobalt(III) ion and that in the case of nickel(II), high-spin complexes a 15-membered macrocycle is most suitable. However, this does not rule out the possibility of the formation of planar complexes of these ions with ligands having larger or smaller macrorings. It has been suggested[12] that nickel can form such complexes even with 12-membered macrorings, but these complexes are in all probability of the low-spin type.

The picture becomes somewhat more complex when the macrocyclic ligand has different donor atoms or donor atoms of the same kind but of different chemical nature (for example amino- and imino-nitrogen atoms). In this case the metal–donor atom bond length will depend on the type of donor atom. In complexes of ligands of this type the metal ion may not be located in the centre of the plane of the donor atoms.

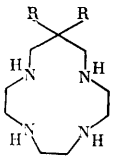
The types of the fundamental structures discovered in transition metal complexes with macrocyclic ligands (henceforth these complexes will be referred to, for brevity, as



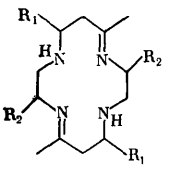
R = H; [12] aneN$_4$(cyclen)
R = $CH_2C_6H_5$; N - $(CH_2C_6H_5)_4$[12] aneN$_4$(tricyclen)



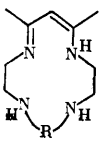
[14] aneN$_4$O$_2$



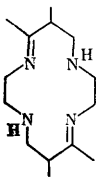
R = H; [13] aneN$_4$
R = CH_3; Me$_2$[13] aneN$_4$



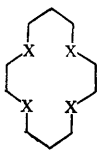
$R_1 = R_2 = H$; Me$_2$[14] 4, 11dieneN$_4$
$R_1 = C_6H_5$; $R_2 = H$; Me$_2$Ph$_2$[14] dieneN$_4$
$R_1 = CH_3$; $R_2 = H$; 5, 7, 12, 14 Me$_4$[14] dieneN$_4$
$R_1 = H$; $R_2 = CH_3$; 3, 5, 10, 12 Me$_4$[14] dieneN$_4$
$R_1 = (CH_3)_2$; $R_2 = H$; Me$_6$[14] dieneN$_4$ (1,7CT)
$R_1 = (CH_3)_2$; $R_2 = CH_3$; Me$_8$[14] dieneN$_4$



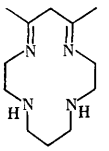
R = $-(CH_2)_2-$; Me$_2$[13] dieneN$_4$
R = $-(CH_2)_3-$; Me$_2$[14] 5, 7 dieneN$_4$



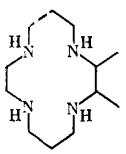
6, 7, 13, 14 Me$_4$[14] dieneN$_4$



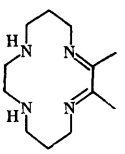
X = NH; [14] aneN$_4$(cyclam)
X = NCH_3; N - Me$_4$[14]aneN$_4$(TMC)
X = S; [14]aneS$_4$



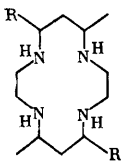
Me$_2$[14] 4,7 dieneN$_4$



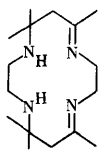
2, 3 Me$_2$[14] aneN$_4$(DMC)



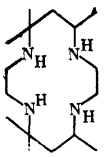
Me$_2$[14] 1,3 dieneN$_4$(DIM)



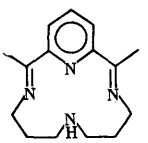
R = H; 5, 12 Me$_2$[14] aneN$_4$
R = C_2H_5; Me$_2$Et$_2$[14] aneN$_4$
R = $(CH_3)_2$; Me$_6$[14] aneN$_4$(tet a/b)



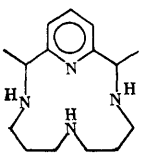
Me$_6$[14] 4,14 dieneN$_4$(1.4CT)



5, 7, 7, 12, 12, 14 Me$_6$[14] aneN$_4$(tet c/d)

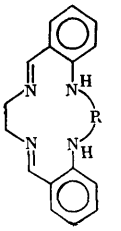


Me$_2$py[14] dieneN$_4$(CR)



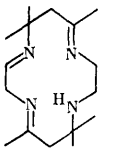
Me$_2$py[14] aneN$_4$(CRH)

Figure 1. The macrocyclic ligands (the numerical indication of the positions of the substituents or double bonds is used only in the presence of several isomers).

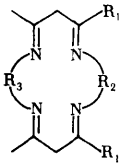


R = —$(CH_2)_2$—; Bz_2[14] dieneN$_4$

R =  ; Bz_2Pyr[14] dieneN$_4$



Me_6[14] trieneN$_4$

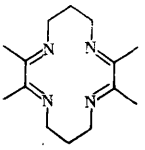


R_1 = H; R_2 = R_3 = —$(CH_2)_2$—; Me_2[14] tetraeneN$_4$

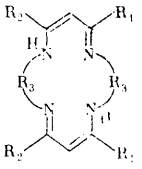
R_1 = H; R_2 = —$(CH_2)_2$—; R_3 = —$(CH_2)_3$—; Me_2[15] tetraeneN$_4$

R_1 = H; R_2 = R_3 = —$(CH_2)_3$—; Me_2[16] tetraeneN$_4$

R_1 = CH_3; R_2 = R_3 = —$(CH_2)_3$—; Me_4[14] 4, 7, 11, 14 tetraeneN$_4$



Me_4[14] tetraeneN$_4$(TIM)

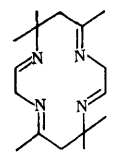


R_1 = R_2 = CH_3; R_3 = —$(CH_2)_2$—; Me_4[14]4, 6, 11, 13 tetraeneN$_4$

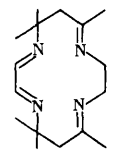
R_1 = R_2 = H; R_3 = —C_6H_4—; Bz_2[14] tetraeneN$_4$

R_1 = H; R_2 = CH_3; R_3 = —C_6H_4—; Me_2Bz_2[14] tetraeneN$_4$

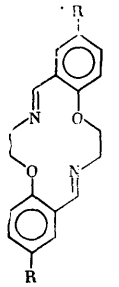
R_1 = R_2 = CH_3; R_3 = —C_6H_4—; Me_4Bz_2[14] tetraeneN$_4$



Me_6[14] tetraeneN$_4$

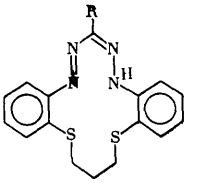


Me_6[14]4, 8, 10, 14 tetraeneN$_4$



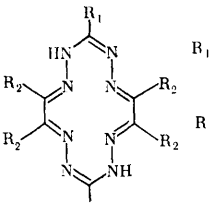
R = H; Bz_2[14] dieneN$_2$O$_2$

R = OCH_3; $(CH_3OC_6H_3)_2$[14] dieneN$_2$O$_2$

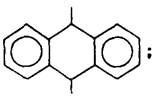


R = H; Bz_2[14] dieneN$_4$S$_2$

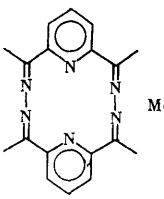
R = $(CH_2)_3OH$; $OprBz_2$[14] dieneN$_4$S$_2$



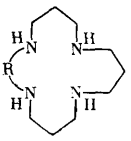
R_1 = H; R_2 = CH_3; Me_4[14] hexaeneN$_8$

R_1 = $(CH_2)_7CH_3$; R_2R_2 =  ;

Oct_2Antr_2[14] hexaeneN$_8$

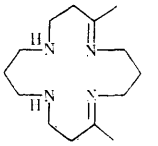


Me_4py_2[14] tetraeneN$_6$

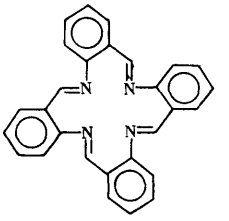


R = —$(CH_2)_2$—; [15] aneN$_4$

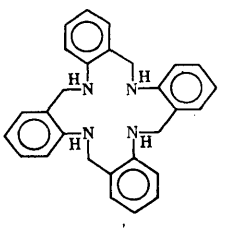
R = —$(CH_2)_3$—; [16] aneN$_4$



Me_3[16] dieneN$_4$



Bz_4[16] tetraeneN$_4$(TAAB)



Bz_4[16] aneN$_4$(TAABH$_8$)

Figure 1 (contd.)

macrocyclic complexes), are presented in Fig.2. Structure A is characteristic of the majority of nickel(II) complexes. Apart from nickel, complexes of this kind have been found only for copper(II)[13,14] and cobalt(II).[15] Structure B is obtained when the diameter of the plane of the macroring is too small for the given metal ion and the rigidity of the ligand prevents it from assuming another conformation more suitable for coordination. For complexes with a coordination number (C.N.) of 5 there is a possibility of structures of types C, D, and E. The structure of the complex in each specific case is determined by the characteristics of the structure of the macrocyclic ligand. Complexes having structure F are probably most common, but their X-ray diffraction analysis has been carried out in only a limited number of instances. Structure G is obtained when additional bidentate and monodentate ligands are involved in coordination apart from the macrocyclic ligands. In the last case[16] the structure is determined by the small size of the macroring, as a result of which the metal ion cannot be accommodated in the centre of the plane of the donor atoms.

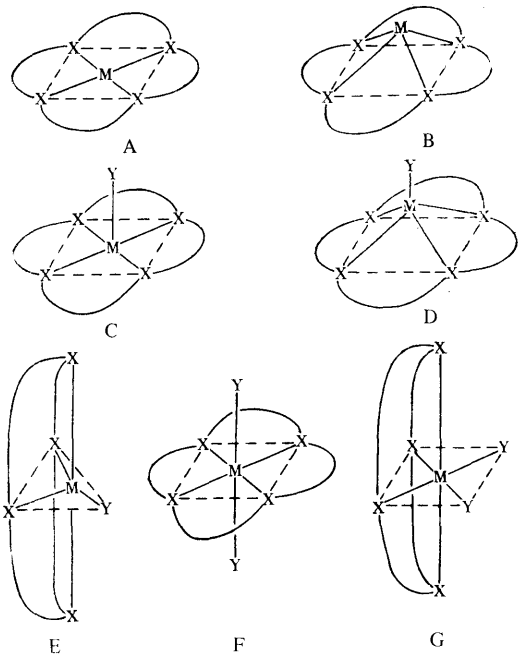


Figure 2. The types of structures of transition metal complexes with macrocyclic ligands (X = donor atoms of macrocyclic ligands; Y = donor atoms of additional ligands).

proton. However, the difference between the last two types of donor atoms is in many cases abolished owing to the conjugation in the six-membered chelate ring. If the complex formation reaction takes place with substitution of a proton at the nitrogen atom, then the imino- and ionic nitrogen atoms become equivalent. Subsequently they will be designated by N_{cov}. The equivalence of these two types of donor atoms in complexes of the above type has been confirmed by X-ray diffraction data (Table 1) and X-ray electronic spectroscopic data[37]. An analogous phenomenon has been observed also in porphyrin and phthalocyanine complexes[38,39]. In all probability the structures of such complexes are represented more correctly by formula I rather than II [in relation to compound No.18 (Table 1)].

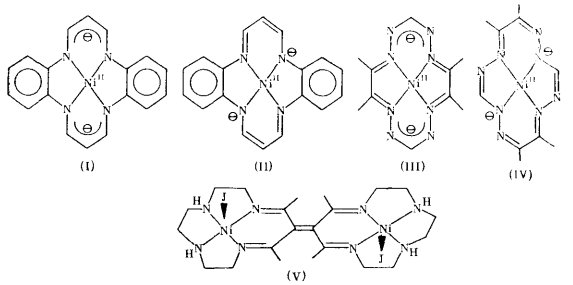


Table 1. The nickel–donor atom distances (in Å) in square planar complexes.

No.	Compound	Ni–N_{am}	Ni–N_{im}	Ni–N_{cov}	Ni–other atoms*	Refs.
1	$Ni(Me_2[13]dieneN_4)ClO_4$	1.88	—	1.83	—	12
2	$Ni(Me_2[13]aneN_4)(ClO_4)_2$	1.87	—	—	—	17
3	$Ni(5,12Me_2[14]aneN_4)(ClO_4)_2$	1.93	—	—	—	18
4	$Ni(Me_2Et_2[14]aneN_4)(ClO_4)_2$	1.98	—	—	—	19
5	$Ni(Me_6[14]aneN_4)(ClO_4)_2$	1.93	—	—	—	20
6	$Ni(Me_2py[14]aneN_4)(ClO_4)_2$	1.88	—	—	1.80 (N_{py})	21
7	$Ni(5,7,12,14Me_4[14]dieneN_4)(ClO_4)_2$	1.93	1.88	—	—	22,23
8	$Ni(3,5,10,12Me_4[14]dieneN_4)(ClO_4)_2$	1.94	1.91	—	—	24
9	$Ni(Me_6[14]4,14dieneN_4)(ClO_4)_2$	1.97	1.89	—	—	25
10	$Ni(Me_6[14]dieneN_4)(ClO_4)_2$	1.90	1.86	—	—	26
11	$Ni(Me_6[14]dieneN_4)(NCS)_2$	1.92	—	—	—	27
12	$Ni(Me_6[14]dieneN_4)(ClO_4)_2$	1.93	1.89	—	—	28
13	$Ni(Bz_2[14]dieneN_4)$	—	—	1.86	—	15
14	$Ni(Bz_2Pyr[14]dieneN_4)$	—	—	1.85	—	15
15	$Ni(Bz_2[14]dieneN_4S_2)ClO_4$	—	—	1.84	2.18 (S)	29
16	$Ni(OprBz_2[14]dieneN_4S_2)ClO_4$	—	—	1.83	2.16 (S)	30
17	$Ni(Me_6[14]4,8,10,14tetraeneN_4)(ClO_4)_2$	—	1.89	—	—	31
18	$Ni(Bz_2[14]tetraeneN_4)$	—	—	1.87	—	32
19	$Ni(Me_2Bz_2[14]tetraeneN_4)$	—	—	1.85	—	33
20	$Ni(Me_4[14]hexaeneN_8)$	—	1.82	—	1.78 (N_{ion})	34
21	$Ni([14]aneS_4)(BF_4)_2$	—	—	—	2.17 (S)	35
22	$Ni(Bz_4[16]tetraeneN_4)(BF_4)_2$	—	1.88	—	—	36

*Here N_{py} is the nitrogen atom of pyridine.

1. Nickel(II) Complexes

The majority of nickel(II) complexes investigated by X-ray diffraction have a square planar structure, although compounds have been found with another structure. Table 1 presents the results of X-ray diffraction studies on the square-planar nickel(II) complexes. The donor atoms in macrocyclic ligands can be oxygen and sulphur atoms, the nitrogen atom N_{am} in a secondary amino-group, the nitrogen atom N_{im} in an imino-group (–CH=N–), and the nitrogen atom N_{ion} coordinated to the metal ion with elimination of a

As was to be expected, the length of the nickel–nitrogen bond depends on the size of the macrocyclic ligand and is shortest in a 13-membered macrocycle (square-planar complexes with twelve-membered macrocycles have not been synthesised). In all cases the Ni–N_{am} bond length is greater than the Ni–N_{im} bond length for the same macrocyclic ligand. This is probably because the imino-group can be involved in the formation of π-bonds as well as a simple donor–acceptor bond, which should enhance the nickel–nitrogen interaction and should lead to the shortening of the distance between these atoms (see also Section IV).

The metal–donor atom bond length is greatly influenced by the structure of the macrocyclic ligand. Thus the Ni–N_{am} and Ni–N_{im} bond lengths in complex No.10 are shorter than in the complex No.9 (Table 1), although the ligands differ only by the relative positions of the imino-bonds and the methyl substituents. The presence of substituents in the ethylenediamine bridge between the donor atoms lengthens the metal–nitrogen bond (cf., for example, complexes No.7 and 8 or complexes No.10 and 12 in Table 1), although the introduction of substituents in the propylenediamine bridge hardly influences the distance (cf. compounds No.3 and 5). The flexibility of the macrocyclic ligand also determines the nickel–nitrogen bond length. Thus the Ni–N_{am} distance in complex No.6 is shorter than the analogous distance in complexes of other 14-membered ligands. The presence of the pyridine ring apparently increases the rigidity of the ligand, which leads to a decrease of the nickel–nitrogen bond length.

The shortest bond between the nickel ion and the nitrogen donor atom among the compounds listed in Table 1 is observed in complex No.20. The ligand forming this complex can be coordinated in two ways [(III) or (IV)]. In the nickel complex version (IV) obtains, so that two types of Ni–N bond are observed. The presence of six double bonds in the macrocyclic ligand molecule decreases the size of its plane, which is reflected in a decrease of the nickel–nitrogen bond length.

It follows from the data in Table 1 that the nickel–nitrogen distance varies consistently as a function of the nature of the donor atom. It increases in the sequence Ni–N_{cov} < Ni–N_{im} < Ni–N_{am}.

The nickel–sulphur distance is virtually constant regardless of which donor atoms, apart from those of sulphur, are coordinated to the nickel ion.

All the compounds in Table 1 are diamagnetic. Certain paramagnetic nickel(II) compounds having C.N. > 4, have now been ivestigated (Table 2). It follows from the data in Tables 1 and 2 that the nickel–nitrogen distance in high-spin complexes is greater than in diamagnetic complexes. The length of this bond increases with the size of the macrocyclic ligand. The Ni–O bond length depends on the charge on the oxygen atom. If it is negative ($acac^-$, CH_3COO^-), the nickel–oxygen distance is shorter than in complexes with neutral oxygen-containing ligands (H_2O), the Ni–$O_{(H_2O)}$ distance being almost independent of the nature of the macrocyclic ligand.

Only two iodide ions, out of the four present, are coordinated in complex No.23 [Table 2 (V)] and the nickel atom has been raised 0.30 Å above the plane of the four nitrogen atoms in the direction of the iodide ion[40]. A similar deviation of the nickel atom from the plane of the donor atoms in the direction of the axial ligand (by 0.33 Å) has been observed also in complex No.27.[44]

Table 2. The metal–donor atom distances (in Å) in high-spin macrocyclic nickel(II) complexes.

No.	Compound	Type of structure[a]	Ni–N_{am}	Ni–N_{im}	Ni–N_{ax}^b	Ni–O	Ni–Hal	Refs.
23	{[Ni(Me_2[13]dieneN$_4$)]I_2}I_2	D	1.92	1.87	—	—	2.96	40
24	[Ni([14]aneN$_4$)Cl$_2$]	F	2.06	—	—	—	2.49	41
25	[Ni(Me_6[14]dieneN$_4$)acac]ClO_4	G	2.11	—	—	2.06	—	42
26	[Ni(Me_6[14]aneN$_4$)CH_3COO]ClO_4	G	2.12	—	—	2.11	—	43
27	[Ni(N-Me_4[14]aneN$_4$)N_3]ClO	D	2.10	—	1.95	—	—	44
28	{Ni[$(CH_3OC_6H_4)_2$[14]dieneN$_2O_2$]I_2}	G	—	2.05	—	2.22	2.73	45
29	[Ni(Br_2[14]dieneN$_2O_2$)I_2]	G	—	1.92	—	2.07	2.88	46
30	[{Ni(N-Me_4[14]aneN$_4$)}$_2N_3$(N_3)$_2$]I	F	2.15	—	2.13	—	—	47
31	[Ni(Me_2[16]dieneN$_4$)Cl, H_2O]Cl	F	2.14	2.10	—	2.22	2.43	48
32	[Ni(Bz_4[16]tetraeneN$_4$)I, H_2O]I	F	—	2.09	—	2.20	2.90	36

Remarks: [a] see Fig.2; [b] N_{ax} = donor nitrogen atom of the axial ligand; acac = acetylacetone.

The presence of the Ni–Ni bond has been demonstrated by X-ray diffraction in complexes with Me_4[14]4,6,11,13-tetraeneN$_4$ and Me_4[14]hexaeneN$_8$ ligands[49]. These diamagnetic coordination compounds have very similar structures and are dimeric both in the solid state and in solution with a nickel–nickel distance of approximately 3 Å. Nickel atoms are raised above the plane of the donor atoms towards one another.

2. Cobalt Complexes

The number of studies on the X-ray diffraction analysis of cobalt complexes of macrocyclic ligands is much smaller than for the nickel complexes. The results obtained are listed in Table 3. The general characteristics observed in the discussion of the stereochemistry of nickel complexes apply also to the cobalt complexes.

Table 3. The metal–donor atom distances (in Å) in certain macrocyclic cobalt complexes.

No.	Compound	Type of structure[a]	Co–N_{am}	Co–N_{im}	Co–N_{cov}	Co–N_{ax}	Co–other atoms	Refs.
33	[Co([12]aneN$_4$)$(NO_2)_2$]Cl	G	1.97	—	—	1.93 (NO_2)	—	16
34	[Co([12]aneN$_4$)CO_3]$ClO_4 \cdot H_2O$	G	1.97	—	—	—	1.92 (O_{CO_3})	50
35	[Co([14]aneN$_4$)en]$Cl_3 . 3H_2O$	G	1.99	—	—	1.98 (en)		51
36	[Co([14]aneN$_4O_2$)ser] $ZnCl_4 \cdot H_2O$	G	1.97	—	—	1.97 (ser)	1.90 (O_{ser})	52
37	[Co([14]aneN$_4$)CH_3, H_2O] $(ClO_4)_2$	F	1.97	—	—	—	2.01 (C_{CH_3}) 2.15 (O_{H_2O})	53
38	[Co(Me_2[14], 4,11dieneN$_4$)$(NCS)_2$] $SCN \cdot H_2O$	F	1.98	2.00	—	1.89 (NCS)		54
39	[Co(Me_6[14]dieneN$_4$)$(NH_3)_2$]$(ClO_4)_3$	F	1.99	1.95	—	1.95 (NH_3)		55
40	[Co(Me_6[14]4,14dieneN$_4$)$(CN)_2$]ClO_4	F	1.97	1.94	—	—	1.92 (C_{CN})	56
41	[Co(Me_2[14]5,7dieneN$_4$)H_2O]$(PF_6)_2$	C	1.99	—	1.92	—	2.28 (O_{H_2O})	57
42	[Co(Me_4[14]tetraeneN$_4$)$(NH_3)_2$]Br_3	F	—	1.90	—	1.97 (NH_3)		58
43	[Co(Me_4Bz_2[14]tetraeneN$_4$)I]$CHCl_3$	D	—	—	1.90	—	2.56 (I)	59
44	[Co([14]aneN$_4$)]$(ClO_4)_2$	A	1.98	—	—	—	—	60
45	[Co(Me_6[14]dieneN$_4$)$(H_2O)_2$]$(BF_4)_2$	F	1.97	1.94	—	—	2.48 (O_{H_2O})	55
46	[Co(Me_4[14]tetraeneN$_4$)$(H_2O)_2$]$(ClO_4)_2$	F	—	1.90	—	—	2.29 (O_{H_2O})	58
47	[Co(Me_4[14]hexaeneN$_8$)CO]	D	—	—	1.87	—	1.77 (C_{CO})	61

Remarks: [a] see Fig.2; en = ethylenediamine; ser = serine.

Table 4. The metal–donor atom distances (in Å) in the macrocyclic complexes of certain transition metals.

No.	Compound	Type of structure[a]	M–N	M–other atoms	M–4N plane	Refs.
48	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)]	B	1.92 (cov)	—	0.11	62
49	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)CO(NH$_2$NH$_2$)]	F	1.94 (cov)	1.75 (C_{CO}); 2,12 ($N_{NH_2NH_2}$)	0.11	63
50	[Fe(Me$_4$py$_2$[14]tetraeneN$_6$)(CH$_3$CN)$_2$](ClO$_4$)$_2$	F	1.89 (im); 190 (c)	1.94 (N_{CH_3CN})	—	64
51	[Fe(Oct$_2$Antr$_2$[14]hexaeneN$_8$)]	A	1.83 (im); 1.85 (ion)	—	—	65
52	[Fe(Me$_6$[14]dieneN$_4$)Cl]I	E	2.17 (am); 2.13 (im)	2.31 (Cl)	—	66
53	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)C$_6$H$_5$]	D	1.91 (cov)	1.93 ($C_{C_6H_5}$)	0.23	67
54	[Fe(Me$_4$Bz$_2$[14]tetraeneN$_4$)Cl]CH$_3$CN	D	2.00 (cov)	2.25 (Cl)	0.60	59
55	[Cu[14]aneN$_4$)](ClO$_4$)$_2$	A	1.95 (am)	—	—	14
56	[Cu([14]aneS$_4$)](ClO$_4$)$_2$	A	—	2.30 (S)	—	13,35
57	{[Cu(Me$_6$[14]dieneN$_4$)]$_2$CN}(ClO$_4$)$_3$	E	2.06 (am); 2.03 (im)	2.13 (N_{CN})	—	68
58	{[Cu(Me$_6$[14]dieneN$_4$)]$_2$Cl}(ClO$_4$)$_3$	E	2.06 (am)[b]; 2.00 (im)[c]	2.50 (Cl)	—	69
59	Mn(Me$_4$Bz$_2$[14]tetraeneN$_4$)NEt$_3$]	D	2.12 (cov)	2.25 (N_{NEt_3})	0.73	59
60	[Cr(Me$_6$[14]dieneN$_4$)NO$_2$, NO]	F	2.04 (am); 2.02 (im)	2.20 (N_{NO_2}); 1,70 (N_{NO})	—	70

Remarks: [a]see Fig.2; [b]distance in trigonal plane; [c]distance to the vertex of the trigonal bipyramid.

Table 3 shows that the Co–N_{am} distance is almost independent of the degree of oxidation of the cobalt ion and remains virtually constant regardless of the mode of coordination of the macrocyclic ligands. Evidently the ability of ligands to form structures with a bent conformation of the macroring (i.e. structures where the donor atoms of the ligand do not occupy the equatorial plane in the coordination sphere of the metal) enables the nitrogen atoms to occupy the most convenient position in relation to the cobalt ion and to avoid strain in the macroring.

As a rule, the Co–N_{am} bond length is greater than the Co–N_{im} bond length. The only exception is complex No.138 (Table 3), which may be accounted for by steric interactions, since in the ligand involved the imino-nitrogen is linked to a carbon atom which is itself joined to a methyl group, while the amino-nitrogen is linked to a carbon atom without alkyl substituents. The cobalt–oxygen distance is determined both by the nature of the macroring and by the characteristics of the axial ligands. The shortest distances are observed when a Co–O ionic bond is formed.

As for the nickel complexes, the equalisation of the Co–N_{im} and Co–N_{ion} bond lengths is observed in the presence of conjugation in the propylene bridge of the macrocyclic ligand. The shortest cobalt–nitrogen distance has been found in complex No.47. The type of coordination of the macrocyclic ligand in the cobalt complexes differs from that in the nickel complex [the cobalt ion is coordinated to the nitrogen atoms of the α-di-imino-groups, as shown in stucture (III)].

3. Other Transition Metal Complexes

A number of iron(II) and iron(III) complexes have been investigated by X-ray diffraction. Some of the results of these investigations are presented in Table 4. The Fe–N distances are various and depend mainly on the type of coordination of the macrocylic ligand and the donor nature of the nitrogen atom. In trigonal-bipyramidal complexes the distance is somewhat greater than in tetragonal compounds.

Comparison of the carbonyl and alkyl derivatives of cobalt and iron shows that, whereas the M–C(CO) distances vary insignificantly [1.77 Å for Co(II) and 1.75 Å for Fe(II)], the M–C(R) distances differ to a greater extent. In complex No.51 (Table 4) the distances between the nitrogen atoms and the iron atom are various, which indicates the absence of the delocalisation of the π-electrons in the propylene bridge (as in complex No.20, Table 1).

The amount of X-ray diffraction data on other macrocyclic complexes is slight (Table 4). Only square-planar[13,14,35] and trigonal-bipyramidal[68,69] structures have been observed for the copper compounds. The structures of the macrocyclic manganese(II) [59] and chromium(I) [70] complexes have also been determined.

Inspection of the data in Tables 1–4 reveals a consistent variation of the metal–nitrogen donor atom distance in complexes of different metals with macrocyclic ligands. In terms of the decrease of the length of the bond, the metals can be arranged in the following sequence†:

$$Fe^{3+}>Fe^{2+}>Ni^{2+}\ (S=1)>Cu^{2+}>Co^{3+}\simeq Co^{2+}>Ni^{2+}\ (S=0)\ .$$

This series holds for any donor nitrogen atom (N_{am}, N_{im}, and N_{cov}). In the nickel complexes the metal–donor atom distance is greatly influenced by the spin state of the metal ion.

III. ABSORPTION SPECTRA OF IRON COMPLEXES

There are literature data on the absorption spectra of different macrocyclic iron(II) and iron(III) complexes which include both high-spin and low-spin compounds. The results of these studies will be considered below.

1. Iron(III) Complexes

In high-spin iron(III) complexes the ground state is ^6S and is not split in a crystal field of any symmetry. Complexes of this type are characterised by a low intensity of the *d–d* transitions, because they all spin-prohibited. In the spectra of the compounds investigated charge-transfer L–Fe^{III} bands have been observed at ~30000 cm^{-1} for halide complexes[71,72] and at ~19000 cm^{-1} for thiocyanate[72] complexes.

The magnetic moments of all these compounds are in the range 5.7–6.1 μ_B. The lower magnetic moments of some of the complexes[72] have been explained by the admixture of the excited ^4E_g and $^2B_{2g}$ states to the $^6A_{1g}$ ground state.

Very few low-spin iron(III) complexes are known and their *d–d* spectra have in general been poorly characterised[73–75]. Their magnetic moments are in the range 2.1–2.3 μ_B. With increase of the number of double bonds in the macrocyclic ligand, a steady decrease of the magnetic moment has been

†Here *S* is the overall spin of the ion.

observed for isotypical complexes: $\mu_{eff} = 2.30$, 2.13, and 2.06 μ_B respectively for *trans*-$[FeLCl_2]^+$, where L = Me_6-[14]dieneN$_4$, Me_6[14]trieneN$_4$ and Me_4[14]tetraeneN$_4$.

It follows from the study of Chan and Poon[72] that the spin state of the iron ion is greatly influenced by the relative positions of the ligands: the complexes $[Fe([14]anN_4)X_2]^+$, where X = NCS^-, Cl^-, or Br^-, are high-spin for the *cis*-disposition of the monodentate ligand and low-spin in the case of the *trans*-coordination.

2. High-Spin Iron(II) Complexes

Among the high-spin complexes of bivalent ions, compounds with coordination numbers of 5 (C_{4v} symmetry) and 6 (D_{4h} symmetry) have been observed. The data on the magnetic moments and the electronic absorption spectra of these compounds are presented in Table 5. In the spectra of complexes of this type one may expect the presence of three bands of the spin-allowed transitions $^5B_1 \leftarrow {}^5B_2$, $^5A_1 \rightarrow {}^5B_2$, and $^5E \leftarrow {}^5B_2$. In practice usually two of these are observed (those with higher energies) as broad bands with a low intensity. The ground state in these complexes is $^5B_2$, as shown by Mössbauer spectroscopy[71]. The square-pyramidal complexes of the type under consideration are probably subject to some trigonal distortion[66].

The $^5B_1 \leftarrow {}^5B_2$ transition is determined in the first place by the very strong field of the macrocyclic ligand, since the energy of the $^5A_1 \leftarrow {}^5B_2$ transition is determined by the nature of the axial ligand. In square-pyramidal macrocyclic iron(II) complex a very marked splitting of the "octahedral" ^5E_g state (~7000 cm^{-1}) is observed, which has been explained by the presence of only one axial ligand and by the unusually strong field of the donor atoms of the macrocycle.

The energy of the $^5B_1 \leftarrow {}^5B_2$ transition in the complexes $[Fe(Me_2py[14]aneN_4)X]^+$, where $X^- = Cl^-$, Br^-, or I^-, increases with decrease of the strength of the field of the axial ligand[71], which may reflect the mutual influence of the ligands in the macrocyclic complexes (see Section VII). In terms of increasing strength of the equatorial field, the macrocyclic ligands can be arranged in the following sequence:

$$Me_2py[14]aneN_4 < Me_6[14]tetraeneN_4 < Me_6[14]dieneN_4.$$

Somewhat unexpectedly the di-imine ligand has a stronger field than the tetraimine ligand (see Section IV). Evidently the introduction of additional imine bonds decreases the size of the macroring and leads to the expulsion of the metal ion from the plane of the donor atoms, which weakens the metal–nitrogen interaction and decreases the strength of the field of the macrocyclic ligand.

The magnetic moments of compounds of this type are in the range 4.95–5.20 μ_B, which is somewhat less than in the hexacoordinate complexes (see below). In all probability the marked splitting of the $^5E_g(O_h)$ state reduces μ_{eff} as a result of the orbital contribution.

The magnetic and spectroscopic data on the iron(II) complexes with C.N. = 6 are listed in Table 5. The majority of these compounds have the *trans*-coordination of the axial ligands; the *cis*-coordination has been postulated for the complexes $[Fe(Me_2py[14]aneN_4)CH_3COO]PF_6$ and $[Fe(Me_6[14].$ $.tetraeneN_4)phen](ClO_4)_2$ due to the bidentate coordination of the additional ligands. The symmetry of the chromophore should be pseudo-octahedral in this case and the presence of a single broadened spin-allowed band due to the $^5E_g \leftarrow {}^5T_{2g}$ transition may be expected in the electronic spectrum. In the spectrum of $[Fe(Me_2py[14]aneN_4)(N_3)_2]$, which the authors[71] believe to have a *trans*-structure, no splitting was observed, because the azide ligand gives rise to a field whose strength is similar to that of the macrocyclic ligand. This hypothesis is supported also by the magnetic moment of the above compound.

Table 5. The magnetic moments and absorption bands of high-spin iron(II) complexes[a].

Compound	μ_{eff}, μ_B	Solvent	$^5A_1 \leftarrow {}^5B_2$	$^5B_1 \leftarrow {}^5B_2$	Refs.
$[Fe(Me_2py[14]aneN_4)Cl]PF_6$	4.95	CH_3NO_2	4.9 (4)	10.8 (4)	71
$[Fe(Me_2py[14]aneN_4)Br]PF_6$	5.11	CH_3NO_2	4.5 (5)	11.0 (5)	71
$[Fe(Me_2py[14]aneN_4)I]PF_6$	5.20	CH_3NO_2	4.2 (5)	11.4 (5)	71
$[Fe(Me_6[14]dieneN_4)Cl]ClO_4$	5.05	CH_3NO_2	4.7 (7)	12.2 (5)	9,76,77
$[Fe(Me_6[14]dieneN_4)Br]ClO_4$	5.11	CH_3NO_2	~5 (~5)	12.5 (5)	9,76,77
$[Fe(Me_6[14]dieneN_5)I]ClO_4$	5.15	CH_3NO_2	~5 (~4)	12.2 (4)	9,76,77
$[Fe(Me_6[14]tetraeneN_4)Cl]ClO_4$	5.00	CH_3NO_2	4.7 (3)	11.6 (3)	73
$[Fe(Me_6[14]tetraeneN_4)Br]ClO_4$	5.14	CH_3NO_2	4.8 (3)	11.7 (3)	73
$[Fe(Me_6[14]tetraeneN_4)I]ClO_4$	5.10	CH_3NO_2	~5	11.7 (3)	73
$[Fe(Me_6[14]aneN_4)Cl_2]$	5.58	$CHCl_3$	5.5 (1)	14.0 (2)	10
$[Fe(Me_6[14]aneN_4)Br_2]$	5.47	$CHCl_3$	5.0 (1)	14.1 (5)	10
$[Fe(Me_6[14]aneN_4)I_2]$	5.37	$CHCl_3$	5.0	14.2 (7)	10
$[Fe(Me_6[14]aneN_4)(CH_3COO)_2]$	5.70	$CHCl_3$	10.7 (1)	14.0 (2)	10
$[Fe(Me_2py[14]aneN_4)(N_3)_2]$	5.50	CH_3NO_2	11.7 (55) b		71
$[Fe(Me_2py[14]aneN_4)CH_3COO]PF_6$	5.11	CH_3OH	11.6 (10) b		71
$[Fe(Me_6[14]tetraeneN_4)phen](ClO_4)_2$	5.00	solid[c]	11.16)		73
$[Fe(13]aneN_4)(NCS)_2]$	5.42	solid[c]	8.8	11.5	78
$[Fe([15]aneN_4)(CH_3CN)_2](PF_6)_2$	5.52	CH_3CN	9.6 (4)	14.1 (4)	78
$[Fe([15]aneN_4)(NCS)_2]$	5.32	$CHCl_3$	10.4 (6)	12.6 (5)	78
$[Fe([16]aneN_4)(CH_3CN)_2](PF_6)_2$	5.55	CH_3CN	9.3 (3)	12.3 (4)	78
$[Fe([16]aneN_4)(NCS)_2]$	5.52	$CHCl_3$	9.1 (1)	11.1 (5)	78

Remarks: [a]here and henceforth the positions of the absorption bands are given in units of 10^3 cm^{-1}, the values of ε, expressed in litre cm^{-1} mol^{-1}, being given in brackets; [b] $^5E_g \leftarrow {}^5T_{2g}$ transition for octahedral symmetry; [c]spectra of compounds in the solid state; phen = phenanthroline.

The positions of the absorption bands in the spectra of these complexes depend, as for the compounds with C.N. = 5, on the strength of the field of the equatorial axial ligands. In the complexes $[Fe(Me_6[14]aneN_4)X_2]$ there is a correlation between the energy of the *d*–*d* transitions and the magnetic moments. With increase of the strength of the field due to the axial ligand, i.e. with increase of the energy of the $^5A_{1g} \leftarrow {}^5A_{2g}$ transition, the $^5B_{1g} \leftarrow {}^5B_{2g}$ band shifts to the low-energy region, which indicates a decrease of the macrocyclic ligand field strength. If the axial ligands are arranged in terms of the increasing splitting of the $^5E_g(O_h)$ state (the $CH_3COO^- < Cl^- < Br^- < I^-$ sequence), then it follows from the data in Table 5 that the magnetic moments of the complexes formed by them decrease in the same direction. This confirms the above hypothesis concerning the contribution of the orbital moment of the μ_{eff} of these compounds.

It follows from the spectra of the complexes $[Fe([X]aneN_4)Y_2]$, where X = 15, or 16 and Y = NCS^- or CH_3CN, that[78] the strength of the field of the macrocyclic ligand is greater in the acetonitrile complexes than in the thiocyanate complexes. Evidently the greater the axial ligand field strength the lower the macrocyclic ligand field strength and conversely. On passing from complexes of a 15-membered ligand to those of a 16-membered ligand the strength of the field due to the macrocycle diminishes by 180 cm^{-1} for the acetonitrile complexes and by 150 cm^{-1} for the thiocyanate complexes.

A series of square planar iron(II) complexes, having the triplet ground state $^3B_{2g}$, have been obtained recently[79]. Their effective magnetic moments are 3.2–4.3 μ_B and their electronic absorption spectra are characterised by the presence of two absorption bands in the ranges 4000–7000 and 12000–15000 cm^{-1}.

3. Low-Spin Iron(II) Complexes

The spin state of iron(II) is determined by both macrocyclic and axial ligands involved in coordination. For example, the complexes [Fe([14]aneN$_4$)X$_2$] are low-spin for X = CH_3CN, NCS^-, or CN^-, while among the complexes of the [15]aneN$_4$ ligand only the cyanide compounds are low-spin[78]. In many instances the absorption spectra of these complexes contain intense charge-transfer of intraligand transition bands, which mask the d–d bands. Such cases will not be considered. A diagram of the states of the low-spin hexacoordinate iron(II) complexes is presented in Fig. 3*a*. Evidently at least four bands due to spin-allowed transitions can be expected in the absorption spectra of the tetragonal complexes of bivalent iron. However, if the splitting of the "octahedral" $^1T_{1g}$ and $^1T_{2g}$ states is not observed, then the absorption spectra of such compounds are interpreted from the standpoint of pseudo-octahedral symmetry. The spectroscopic data for the hexacoordinate low-spin iron(II) complexes are presented in Table 6.

The energy of the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition is $10\,Dq - C$.[80] A method has been developed[81] for the calculation of the crystal field parameters for tetragonal low-spin complexes of ions with the d^6 configuration. According to the results of this study, the energies of the transitions are described by the following equations:

$$E(^1A_{2g} \leftarrow {}^1A_{1g}) = 10Dq^{xy} - C = \nu_2,$$
$$E(^1E_g \leftarrow {}^1A_{1g}) = 10\,Dq^{xy} - 35/4Dt - C = \nu_1,$$
$$Dt = 4/7\,(Dq^{xy} - Dq^z).$$

Hence we have

$$Dq^{xy} = \nu_2 + C,$$
$$Dq^z = Dq^{xy} - 7/4\,Dt,$$
$$Dt = 4/35\,(\nu_2 - \nu_1),$$

where Dq^{xy} (or Dq^E) is the strength of the field due to the equatorial macrocyclic ligand, Dq^z (or Dq^A) is the strength of the field due to the axial ligands, Dt is the tetragonal distortion parameter, and C is the Racah coefficient. If $Dq^{xy} > Dq^z$, then $Dt > 0$ and the sequence of levels corresponds to that illustrated in Fig. 3*a*. If $Dq^{xy} < Dq^z$, then $Dt < 0$ and the ^1E_g level lies above the $^1A_{2g}$ level. This case obtains in the macrocyclic iron(II) complexes with cyanide axial ligands. Having adopted the Racah coefficient $C = 3300$ cm^{-1}, it is possible to calculate from the absorption bands Dq^{xy}, Dq^z, and Dt (Table 6).

Examination of the results shows that Dq^{xy} is influenced by the structure of the macrocyclic ligand. With increase of the number of imino-nitrogen atoms, the parameter increases. The number of methyl substituents in the macroring has a much weaker influence, although as a rule the greater the number of such substituents the smaller Dq^{xy} {cf., for example, the values of Dq^{xy} for [14]aneN$_4$ and Me$_6$[14]aneN$_4$ in the cyanide complexes}.

The strength of the field due to this macrocyclic ligand also diminishes with increase of Dq^z of the axial ligand and conversely. As will be shown subsequently, this phenomenon is characteristic also of the tetragonal cobalt(III) and nickel(II) complexes[83].

With increase of the size of the macrocyclic ligand, the strength of the field generated by it diminishes, which can be seen in relation to the complexes [Fe([X]aneN$_4$)(CN)$_2$], where X = 13, 14, and 15. On passing from a 13-membered to a 14-membered ligand, Dq^{xy} decreases by 180 cm^{-1}; on further increase of the number of members in the ring by unity, Dq^{xy} decreases by 190 cm^{-1}. These values are close to those for the high-spin iron(II) complexes (see above). Hence it follows that the change in the parameters Dq^{xy} with increase of the number of members in the macroring does not depend on the spin state of the iron(II) ion.

The magnetic moments of the tetragonal iron(II) complexes are in the range 0.4–0.8 μ_B, but, one should note that there is a tendency towards an increase of μ_{eff} with decrease of Dq^z.

IV. ABSORPTION SPECTRA OF COBALT COMPLEXES

Among the macrocyclic cobalt(II) complexes, compounds with C.N. = 4, 5, and 6 have been observed. The tetracoordinate complexes are of the low-spin type, while those with C.N. = 6 are of the high-spin type. The vast majority of cobalt(III) complexes are diamagnetic and have C.N. = 6.

1. High-Spin Cobalt(II) Complexes

The spectra of high-spin cobalt complexes show that the metal ion has a pseudo-octahedral environment[84,85]. The spectra are characterised by the presence of three absorption bands in the visible region at 8000, 16000, and 19000 cm^{-1}, which corresponds to the spin-allowed transitions

Table 6. Absorption bands and spectroscopic parameters of low-spin iron(II) complexes with C.N. = 6.

Compound	Solvent	$^1E_g \leftarrow {}^1A_{1g}$	$^1A_{2g} \leftarrow {}^1A_{1g}$	$^1B_{2g}$, $^1E_g \leftarrow {}^1A_{1g}$	Parameters, cm^{-1}			Refs.
					Dq^{xy}	Dq^z	Dt	
[Fe(Me$_6$[14]aneN$_4$)(CN)$_2$]	$CHCl_3$	20.2 (38)	16.1 (5)	26.4 (65) sh	1940	2760	−469	10
[Fe(Me$_2$py[14]aneN$_4$)(NCS)$_2$]	solid	15.6	20.4	—	2370	1410	549	71
[Fe(Me$_6$[14]aneN$_4$)Cl$_2$]	DMF	16.6 (77)	18.9 (88)	—	2220	1760	263	77
[Fe([13]aneN$_4$)(CN)$_2$]	CH_3OH	23.0 (78)	18.8 (65)	27.9 (71)	2210	3050	−480	78
[Fe([14]aneN$_4$)(CN)$_2$]	CH_3OH	21.1 (49)	17.0 (51)	27.3 (110)	2030	2850	−469	78
[Fe([15]aneN$_4$)(CN)$_2$]	CH_3OH	19.6 (27)	15.1 (62)	24.7 (64)	1840	2740	−514	78
[Fe(Me$_6$[14]tetraeneN$_4$)(NCS)$_2$]	solid	16.8	21.7	25.0	2500	1520	560	73,74
[Fe(Me$_6$[14]tetraeneN$_4$)(CH_3CN)$_2$](PF$_6$)$_2$	CH_3CN	15.4 (93)	21.3 sh	26.3 (400)	2460	1280	674	74
[Fe(Me$_4$[14]4,7,11,14tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	12.1 (528)	19.3 (560)	—	2260	830	817	79
[Fe(Me$_2$[16]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	13.5 (20)	19.0 (133)	—	2230	1130	629	79
[Fe(Me$_2$[15]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	13.2 (23)	19.6 (320)	—	2290	1110	731	79
[Fe(Me$_2$[14]tetraeneN$_4$)(py)$_2$](PF$_6$)$_2$	CH_3NO_2	12.4 (580)	20.2 (493)	—	2350	780	903	82
[Fe(Me$_2$[14]tetraeneN$_4$)(NCS$_2$]	THF	15.9 (235)	20.2sh	—	2350	1490	491	82
[Fe(Me$_2$[14]tetraeneN$_4$)(CH_3CN)$_2$])PF$_6$)$_2$	CH_3CN	13.7 (46)	21.3 (105)	—	2460	940	868	82

Remarks: here and henceforth sh = shoulder.

$^4T_{2g} \leftarrow {}^4T_{1g}$, $^4A_{2g} \leftarrow {}^4T_{1g}$, and $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ respectively. The majority of complexes of this type are formed by macrocyclic ligands having nitrogen and oxygen donor atoms. In these complexes the macrocycles have a distorted conformation and the monodentate ligands occupy the *cis*-positions in the octahedron.

The cobalt compounds with the N-$(CH_2C_6H_5)_4$[12]aneN$_4$ ligand are high-spin complexes with a trigonal-bipyramidal coordination[84]. This structure of the complexes is determined by the structure of the macrocyclic ligand, which consists of a 12-membered ring and contains four tertiary nitrogen atoms with bulky substituents. A number of bands have been observed in the absorption spectra of these compounds, but these have not been assigned.

The magnetic moments of both pseudo-octahedral and trigonal-bipyramidal cobalt(II) complexes have values of the order of 4.5–5.0 μ_B, which corresponds to the presence of three unpaired electrons.

2. Low-Spin Cobalt(II) Complexes

Among the low-spin complexes of bivalent cobalt, square-planar, square-pyramidal, and trigonal-bipyramidal compounds have been found.

The square-planar structure of cobalt(II) complexes is formed by virtue of the characteristics of the structures of the macrocyclic ligands. A series of bands due to spin-allowed transitions are observed in the spectra of these compounds. The bands are presented in Table 7.

Since the energy of the $^2A_{2g} \leftarrow {}^2A_{1g}$ transition depends on Dq^{xy}, the relative strength of the field due to the macrocyclic ligands can be inferred from it. It follows from Table 7 that Dq^{xy} increases in the sequence Me$_6$[14]aneN$_4$ < Me$_2$[14]4,7dieneN$_4$ < Me$_6$[14]dieneN$_4$ < Me$_6$[14]dieneN$_4$ < Me$_6$[14]tetraene N$_4$.

In square-pyramidal complexes the energy of the $^2E \leftarrow {}^2A_1$ transition is related to Dq^z. In terms of the decrease of the energy of this band, the axial ligands can be arranged in the sequence $H_2O \cong CH_4CN > Cl^- > Br^- > I^-$, which corresponds to the spectrochemical sequence.

Table 7. Magnetic moments and absorption bands of low-spin cobalt(II) complexes.

Compound	μ_{eff}, μ_B	Solvent	$^2E \leftarrow {}^2A_1$	$^2B_2 \leftarrow {}^2A_1$	Other bands	Refs.
[Co(Me$_6$[14]aneN$_4$)](ClO$_4$)$_2$		DMF	5.6 (6)	20.7 (70)	—	77,86
[Co(Me$_2$[14]4,7dieneN$_4$)](PF$_6$)$_2$	2.05	solid	7.0	21.7	—	57
[Co(Me$_6$[14]dieneN$_4$)](ClO$_4$)$_2$	—	DMF	6.2 (20)	21.8 (100)	28.7 (2500)	77
[Co(Me$_6$[14]dieneN$_4$)](ClO$_4$)$_2$	—	DMF	6.3 (44)	22.4 (130)	29.8 (2500)	77
[Co(Me$_6$[14]tetraeneN$_4$)](ClO$_4$)$_2$	2.12	CH_3NO_2	7.1 (39)	23.8 (257)	28.2 (1840)	87
[Co(Me$_2$[14]5,7dieneN$_4$)I]	1.94	solid	5.8	22.7	30.3	57
[Co(Me$_2$[14]4,7dieneN$_4$)I]I	1.88	solid	5.8	20.8	28.6	57
[Co(Me$_6$[14]tetraeneN$_4$)H$_2$O](ClO$_4$)$_2$	2.09	H_2O	7.9 (37)	23.8 (265)	28.5 (2850)	87
[Co(Me$_6$[14]tetraeneN$_4$)CH$_3$CN](ClO$_4$)$_2$	1.97	CH_3CN	7.8 (76)	24.4 (258)	29.6 (2820)	87
[Co(Me$_6$[14]tetraeneN$_4$)Cl]ClO$_4$	2.13	CH_3CN	7.1 (30)	22.2 (1265)	28.5 sh	87
[Co(Me$_6$[14]tetraeneN$_4$)Br]ClO$_4$	2.02	CH_3CN	6.8 (11)	19.6 sh	31.3 sh	87

Comparison of two cobalt complexes with ligands of identical structure (neutral and monoanionic) showed that the charged ligand has a higher value of Dq^{xy} (by 190 cm^{-1}) than the neutral ligand.

An absorption band at 30000 cm^{-1} is observed in almost all the spectra. It is associated with charge transfer from the metal to the π-antibonding orbital of the imino-group[82].

According to the results of long and Busch[88], the cobalt(II) complexes of Me$_2$py[14]dieneN$_4$ are low-spin and have a trigonal-bipyramidal coordination, but detailed studied on their absorption spectra have not been carried out.

3. Pseudo-Octahedral Cobalt(III) Complexes

According to their spectroscopic properties, all the cobalt(III) complexes can be divided into two large groups: pseudo-octahedral and tetragonal. The pseudo-octahedral complexes can be divided in their turn into compounds containing additional ligands, occupying two *cis*-positions in the octahedron (the macrocyclic ligand then assumes a bent conformation), and tetragonal compounds (with axial ligands in the *trans*-positions), in which the splitting of the "octahedral" absorption band is not observed.

Since the iron(II) and cobalt(II) ions have the same electronic configuration (d^6), the diagrams of their energy levels in octahedral and tetragonal fields are similar (Fig. 3*a*). The transition energies are as follows in the case of the pseudo-octahedral coordination[80]:

$$\nu_1 = E(^1T_{1g} \leftarrow {}^1A_{1g}) = 10\,Dq - C,$$
$$\nu_2 = E(^1T_{2g} \leftarrow {}^1A_{1g}) = 10\,Dq - C + 16\,B,$$

where C and B are Racah coefficients. Having adopted $C = 4B$, it is possible to calculate the parameters of the ligand field:

$$Dq = (3\nu_1 + \nu_2)/40 \quad B = (\nu_2 - \nu_1)/16\ .$$

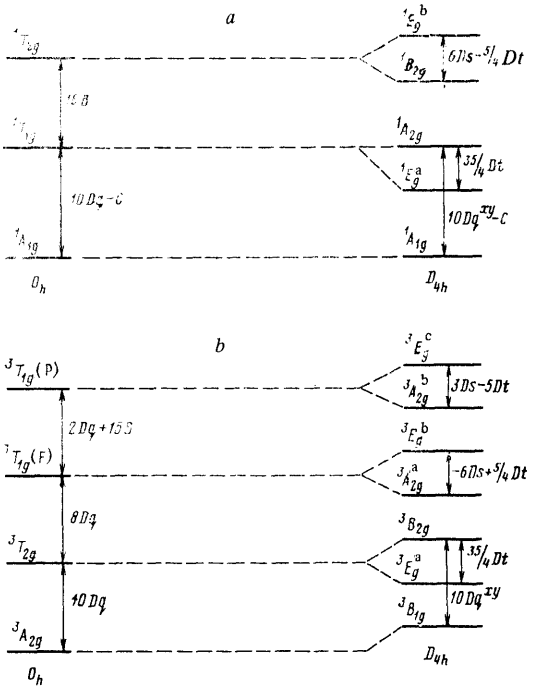


Figure 3. Diagrams and energies of the levels for the low-spin d^6 configuration (*a*) and the high-spin d^8 configuration (*b*) in octahedral (O_h) and tetragonal (D_{4h}) fields (the superscript a, b, and c are used to denote levels of identical symmetry and *Ds* and *Dt* are parameters of the tetragonal distortion).

The spectroscopic parameters of certain pseudo-octahedral complexes are listed in Table 8. They show that all the macrocyclic ligands can be arranged in the following sequence in terms of the decrease of Dq for a fixed bidentate ligand: $Me_6[14]dieneN_4 > 6,7,12,13Me_4[14]dieneN_4 > Me_2py[14]aneN_4 > [12]aneN_4 > Me_6[14]aneN_4 > 5,7,7,12,12,14Me_6[14]aneN_4$.

Comparison of the values of Dq for the oxalate and carbonate complexes shows that $Dq[CoLC_2O_4]^+ > Dq[CoLCO_3]^+$. The difference between them increases in the sequence of ligands $Me_2py[14]aneN_4 < Me_6[14]aneN_4 < [12]aneN_4$. The flexibility of the macroring increases in the same sequence: the pyridine ring in $Me_2py[14]aneN_4$ fixes the two ethylene bridges more rigidly than the six methyl groups in $Me_6[14]aneN_4$ and -[12]aneN$_4$, which have no substituents in the macroring.

The spectra of cobalt(III) complexes with monodentate ligands in the *cis*-positions[91,94,98] are very similar to the spectra of the compounds discussed above.

From the spectroscopic standpoint, the cobalt(III) ammines behave as octahedral compounds (Table 8). According to McClure[99], the splitting of the $^1T_{1g}$ and $^1T_{2g}$ levels in a field of D_{4h} symmetry arises owing to the difference between the σ- and π-antibonding properties of the equatorial and axial donor atoms. In the amine complexes this difference is too small to cause the splitting of the degenerate levels.

The value of Dq for the pseudo-octahedral complexes is determined by the rigidity of the ligand as well as the donor properties of all six atoms coordinated to cobalt. The more flexible the macrocyclic ligand, the much smaller the strain arising when it is coordinated to a cobalt ion, and the greater the overlap of the *d* orbitals of the latter with the orbitals of the donor ligand atoms.

Dq is also influenced by various other parameters: the number of substituents in the macroring and the number of double bonds and their relative positions. The influence of the latter factor is seen particularly clearly when the nephelauxetic coefficients β are compared. In terms of the increase of this parameter, the nitrogen donor atoms have been arranged in the sequence 4N(α-diim) < 2N(α-diim) + 2N(am) < 2N(im) + 2N(am) < 4N(am). This sequence reflects the decrease of the degree of covalence of the metal–nitrogen bond.

Table 8. Absorption bands and spectroscopic parameters of certain pseudo-octahedral cobalt(III) complexes.

Compound	Solvent	$^1T_{1g}\leftarrow{}^1A_{1g}$	$^1T_{2g}\leftarrow{}^1A_{1g}$	Parameters, cm^{-1}			Refs.
				Dq	B	β	
[Co(Me$_6$[14]aneN$_4$)C$_2$O$_4$]ClO$_4$	solid	18.4	25.5	2018	444	0.42	89
[Co(Me$_6$[14]aneN$_4$)CO$_3$]ClO$_4$	solid	18.2	25.4	2000	450	0.42	89
[Co(Me$_6$[14]aneN$_4$)acac](ClO$_4$)$_2$	solid	18.5	26.9	2060	525	0.49	89
[Co(Me$_6$[14]aneN$_4$)NO$_3$](NO$_3$)$_2$	solid	17.1	26.3	1940	575	0.54	89
[Co(Me$_6$[14]aneN$_4$)en]Cl$_3$	solid	18.0	25.8	1995	488	0.46	89
[Co(5,7,7,12,12,14Me$_6$[14]aneN$_4$) × C$_2$O$_4$]ClO$_4$	solid	17.9	26.6	2008	544	0.51	90
[Co(Me$_2$py[14]aneN$_4$)C$_2$O$_4$]ClO$_4$	CH$_3$OH	19.5 (271)	26.7 (329)	2130	450	0.42	91
[Co(Me$_2$py[14]aneN$_4$)CO$_3$]ClO$_4$	H$_2$O	19.3 (292)	27.0 (339)	2123	481	0.45	91
[Co(Me$_2$py[14]aneN$_4$)acac](ClO$_4$)$_2$	H$_2$O	19.7 (301)	26.4 (280)	2138	419	0.39	91
[Co(Me$_2$py[14]aneN$_4$)en](ClO$_4$)$_3$	H$_2$O	20.7 (250)	29.0 (256)	2248	519	0.49	91
[Co(Me$_6$[14]dieneN$_4$)CO$_3$]ClO$_4$	H$_2$O	20.0 (121)	28.6 (135)	2215	538	0.50	92
[Co(6,7,13,14Me$_4$[14]dieneN$_4$)CO$_3$]ClO$_4$	CH$_3$CN	19.8 (126)	26.0 (176)	2135	388	0.36	93
[Co([12]aneN$_4$)C$_2$O$_4$]ClO$_4$	H$_2$O	19.2 (245)	27.4 (205)	2120	513	0.48	94
[Co([12]aneN$_4$)CO$_3$]ClO$_4$	H$_2$O	18.8 (280)	27.2 (210)	2090	525	0.49	94
[Co(6,7,13,14Me$_4$[14]dieneN$_4$)(NH$_3$)$_2$]Cl$_3$	H$_2$O	22.4 (75)	30.0 (118)	2430	475	0.45	93
[Co([14]aneN$_4$)(NH$_3$)$_2$]Cl$_2$	H$_2$O	21.7 (60)	29.0 (70)	2353	456	0.43	95
[Co(Me$_6$[14]aneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	20.6 (75)	28.1 sh	2248	469	0.44	96
[Co(Me$_3$[14]1,3dieneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	22.0 (80)	29.0 (700)	2375	438	0.41	96
[Co(Me$_6$[14]dieneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	22.0 (66)	29.6 (80)	2390	475	0.45	96
[Co(Me$_4$[14]tetraeneN$_4$)(NH$_3$)$_2$](ClO$_4$)$_3$	H$_2$O	23.1 (120)	28.6 sh	2448	344	0.32	96
[Co(5,7,12,14Me$_4$[14]dieneN$_4$) × (NH$_3$)$_2$]Cl$_2$ClO$_4$	H$_2$O	21.8 (74)	29.4 (92)	2370	475	0.45	97

Note: β = nephelauxetic coefficient.

4. Tetragonal Cobalt(III) Complexes

From the point of view of composition, complexes of this type can be divided into three large groups. The first group includes compounds formed by a macrocyclic ligand and two identical axial ligands. The composition of complexes of the second group includes two different axial ligands, while the complexes of the third group are characterised by the presence of an axial cobalt–carbon σ-bond and the second axial ligand can be both an anion (Cl^-, Br^-, I^-, NCS^-, or CN^-) and a neutral molecule (PPh_3, py, CH_3CN, or H_2O).

The splitting of the band due to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition is observed in the spectra of all these compounds. In certain cases the higher-energy "octahedral" band is also split. This makes it possible to calculate the parameters Dq^{xy}, Dq^z, and Dt by the method described in the discussion of iron(II) complexes[81]. The Racah coefficient C for the cobalt(III) ion was assumed to be 3800 cm^{-1}.

Table 9 presents data on the absorption spectra of complexes of the first group and their spectroscopic parameters are given below in Tables 13 and 14. The tetragonal cobalt complexes of this type are ideal objects for the investigation of the influence of various factors, particularly the structure of macrocyclic ligands, on the spectroscopic parameters. Busch and coworkers[101] investigated the dependence of Dq^{xy} on the degree of unsaturation of the macrocyclic ligand in relation to the bis(acetonitrile) complexes with 14-membered ligands. Their data show that Dq^{xy} increases with the

Table 9. Absorption bands of certain tetragonal cobalt(III) complexes of the type $[CoLX_2]^{n+}$.

L	X	Solvent	$^1E_g\leftarrow{}^1A_{1g}$	$^1A_{2g}\leftarrow{}^1A_{1g}$	$^1T_{2g}\leftarrow{}^1A_{1g}$	Refs.
Me$_6$[14]dieneN$_4$	H$_2$O	H$_2$O	17.3 (24)	24.2 sh	—	100
Me$_6$[14]dieneN$_4$	Cl$^-$	CH$_3$OH	16.0 (46)	22.4 sh	—	100
Me$_6$[14]dieneN$_4$	Br$^-$	CH$_3$OH	15.0 (65)	23.0 sh	31.6 sh	100
Me$_6$[14]tetraeneN$_4$	CH$_3$CN	CH$_3$CN	20.6 (47)	24.0 (72)	27.2 (31)	101
Me$_6$[14]tetraeneN$_4$	Cl$^-$	CH$_3$CN	16.7 (52)	—	—	73,87
Me$_4$[14]tetraeneN$_4$	Br$^-$	CH$_3$CN	15.8 (87)	25.6 (3470)	—	73,87
Me$_4$[14]tetraeneN$_4$	H$_2$O	solid	17.4	24.0	—	102,103
Me$_4$[14]tetraeneN$_4$	Cl$^-$	CH$_3$CN	17.4 (46)	23.3 (144)	—	104
Me$_4$[14]tetraeneN$_4$	CH$_3$CN	CH$_3$CN	20.8 (82)	25.5 (137)	30.4 (294)	101
Me$_4$[14]tetraeneN$_4$	Br$^-$	solid	16.7	22.2	—	102
Me$_2$[14]1,3dieneN$_4$	H$_2$O	H$_2$O	18.2 (35)	23.6 sh	—	102
Me$_2$[14]1,3dieneN$_4$	Cl$^-$	solid	16.2	23.5	—	104
Me$_2$[14]1,3dieneN$_4$	NCS$^-$	H$_2$O	19.2 (435)	21.9 (155)	—	105
Me$_2$[14]1,3dieneN$_4$	Br$^-$	solid	16.4	23.0	—	102
Me$_2$[14]1,3dieneN$_4$	CH$_3$CN	CH$_3$CN	20.6 (106)	24.1 (94)	28.1 (80)	101
[14]aneN$_4$	H$_2$O	H$_2$O	17.5 (67)	23.3 (84)	—	95,106
[14]aneN$_4$	OH$^-$	H$_2$O	18.9 (97)	21.3 (105)	—	95,106
[14]aneN$_4$	Cl$^-$	H$_2$O	15.7 (32)	22.7 (142)	—	107
2,3Me$_2$[14]aneN$_4$	Cl$^-$	CH$_3$OH	16.0 (112)	22.0 (112)	26.2 (135)	104
2,3Me$_2$[14]aneN$_4$	CH$_3$CN	CH$_3$CN	21.1 (129)	23.3 (41)	26.7 (102)	101
Me$_2$py[14]aneN$_4$	H$_2$O	H$_2$O	17.9 (29)	22.1 (245)	—	91
Me$_2$py[14]aneN$_4$	CN$^-$	H$_2$O	25.0 (84)	21.5 (151)	32.7 (315)	91
Me$_2$py[14]aneN$_4$	Cl$^-$	CH$_3$OH	16.2 (44)	21.2 (181)	25.9 (148)	91
Me$_2$py[14]aneN$_4$	NCS$^-$	H$_2$O	19.3 (393)	21.0 (364)	—	91
Me$_2$py[14]aneN$_4$	Br$^-$	CH$_3$OH	15.2 (60)	20.8 (183)	—	91
Me$_2$py[14]aneN$_4$	OH$^-$	H$_2$O	17.0 (29)	20.1 (152)	—	91
Me$_2$py[14]aneN$_4$	CH$_3$CN	CH$_3$CN	21.8 (331)	—	27.3 (266)	101
Bz$_4$[16]tetraeneN$_4$	Cl$^-$	solid	15.6	20.2	26.3; 28,2	108
Bz$_4$[16]tetraeneN$_4$	NCS$^-$	solid	16.6	19.7	29.0	108
Bz$_4$[16]tetraeneN$_4$	Br$^-$	solid	14.4	20.0	27.0	108
Bz$_4$[16]tetraeneN$_4$	N_3^-	solid	15.6	18.5	26.3	108
Me$_6$[14]aneN$_4$	H$_2$O	solid	16.6	21.6	27.5	107
Me$_6$[14]aneN$_4$	CN$^-$	solid	23.2	20.9	28.7	107
Me$_6$[14]aneN$_4$	Cl$^-$	H$_2$O	15.6 (31)	20.7 (35)	24.6 (50)	100
Me$_6$[14]aneN$_4$	NCS$^-$	solid	18.7	20.0	24.0; 26,7	107
Me$_6$[14]aneN$_4$	Br$^-$	H$_2$O	14.7 (45)	20.0 sh	25.1; 28,0	107
Me$_6$[14]aneN$_4$	OH$^-$	solid	16.6	18.9	24.9; 26,6	109
Me$_6$[14]aneN$_4$	CH$_3$CN	CH$_3$CN	20.3 (64)	22.2 (74)	25.8 (66)	101

number of double bonds in the macroring, which confirms the hypothesis that the amino-nitrogen is a more effective donor than the imino-nitrogen. This can be explained by the strong π-electronic interaction between the metal ion and the nitrogen donor atom: the rehybridisation of the unshared electron pair of the nitrogen, accompanying the conversion of the amine into the imine, should have a significant influence on Dq^{xy}. The fact that this parameter is virtually the same for the conjugated and non-conjugated tetraimines {cf., for example, the complexes with Me_4[14]tetraeneN$_4$ and Me_0[14]tetraeneN$_4$ or the di-imines Me_2[14]1,3dieneN$_4$ and Me_6[14]dieneN$_4$} shows that the reverse π-bond is not the main cause of the increase of Dq^{xy} when an amine is replaced by an imine. In all probability, the increase is caused by changes in the nature of the metal–nitrogen σ-bond. The decrease in ring size owing to the larger number of double bonds also makes a definite contribution to the increase of Dq^{xy} for imine ligands compared with amine ligands. Evidently the strengthening of the metal–nitrogen bond due to the π-electronic interaction and the decrease of the size of the macroring make the Co–N$_{im}$ distance shorter than the Co–N$_{am}$ distance (see Section II).

Regardless of the nature of the axial ligands, Dq^{xy} for macrocyclic ligands diminishes in the following sequence as a function of the nature of the nitrogen donor atoms: 4N(α-diimine) ≥ 4N(isolated imine) > 2N(α-diimine) + 2N(amine) ≅ *trans*-2N(imine, 6-membered ring) + 2N(amine) > *trans*-2N-(imine, five-membered ring) + 2N(amine) ≅ *cis*-2N(imine, six-membered ring) + 2N(amine) ≅ N(imine) + 3N(amine) > 4N(amine). In all probability this sequence of donor atoms is characteristic of all transition metals. The increase of Dq^{xy} in the sequence an < diene < tetraene for tetragonal iron(II) complexes had been noted previously and the same sequence is characteristic of nickel(II) complexes (see below).

Me_2py[14]dieneN$_4$ and Me_2py[14]aneN$_4$ are somewhat isolated in this series of macrocyclic ligands. Dq^{xy} for [Co(Me_2py[14]dieneN$_4$)(CH$_3$CN)$_2$](ClO$_4$)$_3$ is greater than for the analogous complex with Me_4[14]tetraeneN$_4$. This effect cannot be explained exclusively by the donor properties of the pyridine nitrogen atom, because the values of Dq^{xy} for the cobalt(III) complexes of Me_2py[14]aneN$_4$ are close to those of the 2,3Me_2[14]aneN$_4$ complexes, while in the case of the nickel(II) complexes they resemble those for the complexes of saturated 14-membered ligands. In this instance a considerable increase of Dq^{xy} for the complexes of the Me_2py[14]dieneN$_4$ ligand can be explained by the conjugation between the pyridine ring and the α-di-imine groups of the macroring, which probably greatly increases the strength of the field due to this ligand.

The study of the influence of the size of the macroring on the spectroscopic properties of cobalt(III) complexes of the type [Co([X]aneN$_4$)Cl$_2$]ClO$_4$, where X = 13, 14, 15, and 16, showed[110] that Dq^{xy} increases with decrease of the size of the macroring. The authors of this study calculated the strain energy arising on coordination of the metal ion to the macrocyclic ligand. It is of interest to note that the Dq^{xy} are not correlated with the strain energy: Dq^{xy} increases in the sequence [16] < [15] < [14] < [13], while the sequence based on the decrease of the strain energy is [16] > [15] > [14] > [13]. Two important conclusions follow from this: (a) Dq^{xy} is related to the ratio of the sizes of the metal ion and the cavity within the macrocycle to a greater extent than to the overall strain energy of the ligand caused by coordination; (b) a 14-membered macrocycle is most suitable as regards size for the cobalt(III) ion.

The absorption spectra of cobalt complexes with two different axial ligands[90,91,95,105,107,108,111] resemble the spectra of the compounds discussed above.

Complexes with an axial cobalt–carbon σ-bond represent an interesting class of coordination compounds. They model vitamin B$_{12}$ and their spectra are typical for tetragonal cobalt complexes and are presented in Table 10 together with certain calculated parameters. The large extinction coefficients of the absorption bands of these compounds can be explained by the high degree of covalence of their bonds. The parameters Dq^z(R) were calculated from the spectra in accordance with the additive rule $Dq^z(X+R) = \frac{1}{2}[Dq^z(X) + Dq^z(R)]$ subject to the condition that the values of Dq^z for CH$_3$CN, NCS$^-$, H$_2$O, Cl$^-$, Br$^-$, and I$^-$ are 2180, 2000, 1720, 1460, 1300, and 1000 cm^{-1} respectively.

Table 10. Absorption bands and spectroscopic parameters of cobalt complexes of the type [CoLRX]$^{n+}$.

R	X	Solvent	$^1E_g \leftarrow {}^1A_g$	$^1A_{2g} \leftarrow {}^1A_{1g}$	Parameters, cm^{-1}				Refs.
					Dq^{xy}	Dt	$Dq^z(X+R)$	$Dq^z(R)$	
L = Me_4[14]tetraeneN$_4$									
CH_3^-	CH$_3$CN	CH$_3$OH	20.5 (2000)	23.8 (1450)	2760	377	2100	2020	112
CH_3^-	H$_2$O	H$_2$O	20.6 (2200)	23.8 (1400)	2760	366	2120	2780	103
CH_3^-	NCS$^-$	H$_2$O	20.6 (1570)	23.8 (1620)	2760	366	2120	2240	103
CH_3^-	Cl$^-$	(CH$_3$)$_2$CO	20.0 (2300)	24.2 (4600)	2800	480	1960	2570	112
CH_3^-	Br$^-$	(CH$_3$)$_2$CO	20.3 (2900)	24.8пл	2860	514	1960	2740	112
CH_3^-	I$^-$	(CH$_3$)$_2$CO	20.0 (4300)	25.0 (8500)	2880	571	1880	2860	112
$CH_2C_6H_5^-$	Cl$^-$	(CH$_3$)$_2$CO	19.9 (1700)	24.1 (4500)	2790	480	1950	2550	112
$CH_2C_6H_5^-$	Br$^-$	(CH$_3$)$_2$CO	19.6 (1600)	24.4 (4500)	2820	549	1860	2540	112
$CH_2C_6H_5^-$	I$^-$	(CH$_3$)$_2$CO	20.2 (2400)	23.8 (6000)	2760	411	2040	3180	112
$CH_2C_6H_5^-$	CH$_2$CN	CH$_3$OH	19.3 (2600)	23.7 (6000)	2750	503	1870	1560	112
L = Me_2py[14]dieneN4									
CH_3^-	—	CH$_3$OH	16.1 (525)	20.6 (1200)	2440	514	1540	3080	113
CH_3^-	Br$^-$	CH$_3$OH	20.4 (1050)	21.4 sh	2520	114	2350	3460	113
CH_3^-	H$_2$O	CH$_3$OH	20.6 (980)	21.8 sh	2560	137	2330	2940	113
$C_2H_5^-$	—	CH$_3$OH	15.7	20.5	2430	549	1470	2940	113

Compared with truly tetragonal complexes (i.e. complexes with identical axial ligands), in these compounds there is an additional factor which determines the value of Dq^z(R). Together with the influence of the macrocyclic ligand on Dq^z(R), the nature of the *trans*-axial ligand has also an effect. The maximum values of Dq^z have been obtained for compounds in which a second axial ligand is absent. In the presence of any *trans*-axial ligand Dq^z(R) is less than the maximum value. The values of this parameter can therefore be used as characteristics of the *trans*-influence of the ligands in macrocyclic complexes.

In compounds of the same macrocyclic ligand the *trans*-influence series of axial ligands in relation to the alkyl group is as follows {for example, for Me_4[14]tetraeneN$_4$ complexes}:

$$CH_3CN > NCS^- > Cl^- > Br^- > H_2O > I^-.$$

Some complexes do not show a splitting of the low-energy band and they can therefore be regarded as pseudo-octahedral. The values of β for these compounds are in the range 0.31–0.39, which confirms the high degree of covalence of their bonds.

V. SPECTRA OF NICKEL(II) COMPLEXES

Among nickel complexes with macrocyclic ligands, both high-spin and low-spin compounds have been found. All the low-spin complexes have a square-planar structure. The coordination number in the high-spin complexes is 5 or 6. From the standpoint of the symmetry of the chromophore, the pentacoordinate compounds can be classified as square-pyramidal (C_{4v}) or trigonal-bipyramidal (D_{3h}) complexes, while complexes with C.N. = 6 are pseudo-octahedral (O_h) or tetragonal-bipyramidal (D_{4h}).

1. Low-Spin Complexes

Depending on the relative strength of the field due to the axial and equatorial ligands, the ground state in the nickel(II) complexes (configuration d^8) can be both $^3B_{1g}$ (tetragonal high-spin complexes) and $^1A_{1g}$ (square-planar low-spin complexes). In the classical phthalocyanine and porphyrin compounds[114] the axial ligands are unable to compete with the strong field generated by the macroring and the triplet ground state of the nickel(II) ion does not occur. Synthetic macrocyclic ligands have Dq^{xy} smaller than for porphyrins but sufficiently large to form mainly low-spin complexes.

In nickel complexes of this type there is a possibility, in principle, of three spin-allowed transitions[80]. All the low-spin complexes which have been discovered have an absorption band in the range 18500–24000 cm^{-1} with an intensity of 20–500 litre cm^{-1} mol^{-1}, which the majority of investigators assign to the $^1A_{2g} \leftarrow {}^1A_{1g}(b_{1g} \leftarrow b_{2g})$ transition[92,93,97,115–153]. In a number of instances a band due to a second d–d transition has been observed in the range 25000–28000 cm^{-1}.[115–118] However, one should note that, if the assignment of the first band is correct, then its energy should correspond to $10Dq^{xy}$, but it has been found that the position of this band depends greatly on many factors—the non-coordinated anion, the ligand conformation, the solvent, the conditions used in the recording of the spectra, etc.

2. High-Spin Complexes

As already mentioned, square-pyramidal and trigonal-bipyramidal high-spin nickel(II) complexes with C.N. = 5 have been found. The absorption spectra of compounds of this type are characterised by the presence of four (rarely five) low-intensity absorption bands[119,154,155] due to transitions between split "octahedral" levels in a field of C_{4v} symmetry[80]. The magnetic moments of these complexes are in the range 2.80–3.20 μ_B.

The trigonal-bipyramidal nickel complexes have been obtained only with the alkylated macrocyclic ligands N-$(CH_2C_6H_5)_4$[12]aneN$_4$ [156] and N-Me_4[14]aneN$_4$.[120,157] The spectra of these complexes have at least five bands due to d–d transitions in the range 6000–25000 cm^{-1}, but the bands have not been assigned.

Nickel(II) complexes with C.N. = 6 can be divided, like the cobalt(III) complexes, into two large groups: pseudo-octahedral and tetragonal. The energy level diagrams for complexes of these types are presented in Fig. 3*b*. In terms of the one-electron approximation, the transition energies in the field of octahedral symmetry are as follows:

$$\nu_1 = E(^3T_{2g} \leftarrow {}^3A_{2g}) = 10\,Dq,$$
$$\nu_2 = E(^3T_{1g} \leftarrow {}^3A_{2g}) = 18\,Dq,$$
$$\nu_3 = E(^3T_{1g}(P) \leftarrow {}^3A_{2g}) = 12\,Dq + 15\,B.$$

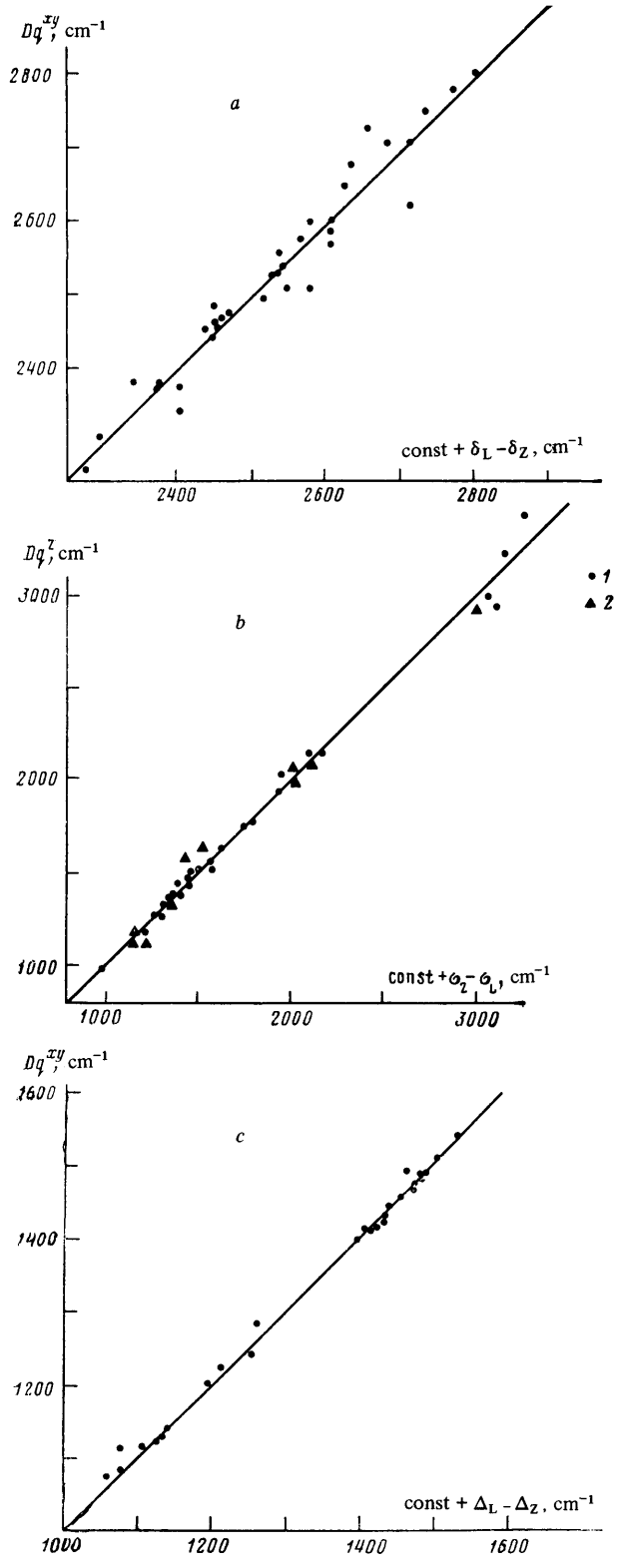


Figure 4. Correlation between Dq_{calc} and Dq_{exp}: *a*) for the values of Dq^{xy} in cobalt(III) complexes; *b*) for the values of Dq^z in cobalt(III) complexes [1) experimental points; 2) points obtained with the aid of Dq^{xy}_{calc}]; *c*) for the values of Dq^{xy} in nickel(II) complexes.

Numerous pseudo-octahedral nickel(II) complexes with macrocyclic ligands have been obtained and characterised[121-126,156-164]. Two or three bands due to *d*–*d* transitions have been observed in the spectra of these compounds in the ranges 10000–12000 (ν_1), 17000–19000 (ν_2), and 27000–29000 cm^{-1} (ν_3) with low extinction coefficients (10–40 litre cm^{-1} mol^{-1}). The values of *Dq* for compounds of this type are in the range 1000–1200 cm^{-1} and are independent of the macrocyclic ligand; they are typical for the amine complexes of nickel(II) and this also applies to the parameters β.

Among the complexes of the same macrocyclic ligand with different bidentate ligands, the highest value of *Dq* and the lowest of μ_{eff} have been found for the oxalate complexes[121], which are dinuclear compounds. Their magnetic moment is reduced owing to the Ni–Ni interaction via the $C_2O_4^{2-}$ bridge group.

A series of hexacoordinate complexes containing *cis*- and *trans*-monodentate ligands have also been isolated[122,123,157,161-163]. It is noteworthy that macrocyclic ligands containing nitrogen and sulphur donor atoms apparently have a low value of Dq^{xy}, since their complexes with Br^- and I^- ligands in the *trans*-positions do not show a splitting of the low-energy band[161,162].

Tetragonal distortion of the complexes entails the splitting of the degenerate levels (Fig. 3*b*), which permits the calculation of the parameters of the tetragonal field from the following formulae:

$$Dq^{xy} = 1/10E(^3B_{2g} \leftarrow {}^3B_{1g}),$$

$$Dt = {}^4/_{35}[E(^3B_{2g} \leftarrow {}^3B_{1g}) - E(^3E_g^a \leftarrow {}^3B_{1g})],$$

$$Dq^z = {}^1/_{10}[2E(^3E_g^a \leftarrow {}^3B_{1g}) - E(^3B_{2g} \leftarrow {}^3B_{1g})].$$

Table 11. Absorption bands of certain tetragonal nickel(II) complexes of the type $[NiLX_2]$ (in the solid state).

L	X	$^3E_g^a \leftarrow {}^3B_{1g}$	$^3B_{2g} \leftarrow {}^3B_{1g}$	$^3A_{2g}^a$, $^3E_g^b \leftarrow {}^3B_{1g}$	$^3A_{2g}^b$, $^3E_g^c \leftarrow {}^3B_{1g}$	Refs.
Me_2Ph_2[14]dieneN$_4$	NO_3^-	9.4	15.6	20.1	—	125
Me_2Ph_2[14]dieneN$_4$	Cl^-	9.3	15.4	19.8	—	125
Me_2Ph_2[14]dieneN$_4$	CH_3COO^-	10.1	15.1	19.9	—	125
Me_2Ph_2[14]dieneN$_4$	NCS^-	10.5	14.7	19.8	—	125
Me_6[14]aneN$_4$	CH_3COO	9.8	16.3	18.4	27.4	158
Me_6[14]aneN$_4$	Br^-	7.4	15.0	12.9; 19.0	26.2; 28.3	167
Me_6[14]aneN$_4$	Cl^-	8.4	14.7	15.1; 19.0	26.7; 28.7	167
Me_6[14]aneN$_4$	N_3^-	9.4	14.1	15.6; 19.5	29.8	167
Me_6[14]aneN$_4$	NCS^-	11.0	14.0	17.3; 20.0	29.8; 30.5	167
Bz$_4$[16]tetraeneN$_4$	N_3^-	10.0	14.7	17.0; 20.0	—	167
Bz$_4$[16]tetraeneN$_4$	NCS^-	10.9	14.7	17.4; 20.0	—	167
[14]aneN$_4$	Br^-	7.9	14.9	13.7; 19.3	27.1; 29.3	167
[14]aneN$_4$	Cl^-	8.6	14.8	15.2; 19.4	27.3; 29.2	167
[14]aneN$_4$	N_3^-	10.1	14.5	16.3; 19.8	—	167
[14]aneN$_4$	NCS^-	11.1	14.2	17.8; 20.2	—	167
2,3Me$_2$[14]aneN$_4$	Br^-	7.8	14.9	13.7; 19.3	27.0; 29.2	167
2,3Me$_2$[14]aneN$_4$	Cl^-	8.4	14.7	15.0; 19.2	27.1; 29.0	167
2,3Me$_2$[14]aneN$_4$	N_3^-	10.1	14.3	16.6; 19.6	—	167
2,3Me$_2$[14]aneN$_4$	NCS^-	11.2	14.1	18.0; 20.2	—	167
[15]aneN$_4$	Br^-	8.1	12.8	13.9; 17.5	25.5; 27.1	167
[15]aneN$_4$	Cl^-	8.7	12.4	14.4; 17.6	26.1; 27.3	167
[15]aneN$_4$	N_3^-	9.7	12.3	15.5; 17.8	27.5	167
[15]aneN$_4$	NCS^-	10.3	12.0	15.8; 18.4	28.5	167
[16]aneN$_4$	Br^-	7.3	11.3	13.1; 15.6	25.6	167
[16]aneN$_4$	Cl^-	7.8	11.2	13.5; 15.8	25.6	167
[16]aneN$_4$	N_3^-	9.0	10.9	14.7; 16.5	26.8	167
[16]aneN$_4$	NCS^-	9.6	10.7	15.4; 16.8	27.1	167
Bz$_4$[16]aneN$_4$	NCS^-	10.1	11.3	15.8; 17.4	28.0	167
Bz$_4$[16]aneN$_4$	Br^-	9.4	11.4	16.4	—	168
Bz$_4$[16]aneN$_4$	Cl^-	9.6	11.3	15.8	—	168

Remarks: for the designation of the energy levels, see Fig. 3*b*.

The absorption bands of tetragonal complexes of this type are presented in Table 11 (the parameters obtained from these spectra are compiled in Table 15). A series of tetragonal complexes, not listed in Table 11, have been obtained also for other macrocyclic ligands[119,122,123,127-130,161,165,166].

As for cobalt(III) complexes, the Me_2py[14]dieneN$_4$ ligand gives rise to the highest value of Dq^{xy} (1866 cm^{-1}) [167] among all the ligands investigated.

Dq^{xy} depends on the size of the macroring: [14]aneN$_4$ (1460 cm^{-1}) > [15]aneN$_4$ (1240 cm^{-1}) > [16]aneN$_4$ (1100 cm^{-1}) (the average values of Dq^{xy} were used, see Table 15). According to the data of Busch and coworkers[167], Dq^{xy} for the "ideal" Ni–N distance is 1213 cm^{-1}. The [15]aneN$_4$ ligand has a value of Dq^{xy} closest to the above (Table 15), which confirms the earlier hypothesis[11] that a 15-membered macroring is optimal for the high-spin nickel(II) ion.

As already mentioned, the introduction of electron-donating imino-groups instead of the amino-groups increases Dq^{xy}. Increments have been proposed[167] for the calculation of the values of Dq^{xy} from a specific value of this parameter—in the given instance from Dq^{xy}{[15]aneN$_4$}, as the most suitable for the high-spin nickel(II) ion. These increments are +210 cm^{-1} when a 15-membered ring is replaced by a 14-membered ring and −130 cm^{-1} when a 15-membered ring is replaced by a 16-membered ring; the replacement of the amino-group by an imino-group increases Dq^{xy} by 75 cm^{-1} for the first and second amino-groups, while the replacement of the third and fourth amino-nitrogen atoms by imino-nitrogen atoms increases Dq^{xy} by 155 cm^{-1}. The latter is due to the more marked decrease of the size of the macroring after the introduction of the third and fourth imino-groups compared with the introduction of the first and (or) the second.

The influence of the axial ligands on the Dq^{xy} parameters is examined below (see Section VII).

V. SPECTRA OF OTHER TRANSITION METAL COMPLEXES

Among the complexes of other transition metals, those of copper(II) have been most fully investigated. Unfortunately, the spectra of these compounds are characterised by a small number of broad absorption bands, which greatly diminishes the possibility of deriving information about them.

The absorption spectra of the majority of compounds investigated contain one broad band in the range 16000–20000 cm^{-1} with extinction coefficients of 50–200 litre cm^{-1} mol^{-1}.[92,93,97,125,130-133,169-176] There is apparently no direct correlation between the strength of the field due to the macrocyclic ligand and the position of this band, although an interesting relation has been observed[77] between the position of the above absorption band and the heat of formation of amine complexes of copper.

In a number of instances two[120,134,135,178] or even three[140] absorption bands have been observed in the spectra, but the amount of data is too small to make a correct assignment of these bands.

A square-pyramidal[171,179-181] or trigonal-bipyramidal[155] structure has been proposed for certain pentacoordinate copper compounds, the latter structure having been confirmed by X-ray diffraction[69]; however, the absorption bands were not assigned in the above studies.

Data on the absorption spectra of compounds of other transition metals are presented in Table 12. It is noteworthy that the energies of the $^4B_{2g} \leftarrow {}^4B_{1g}$ (for the d^3 configuration) and $^5B_{2g} \leftarrow {}^5B_{1g}$ (for the d^4 configuration) transitions correspond to values of $10Dq^{xy}$, which makes it possible to follow the variation of this parameter along the series

of transition metals. For compounds of the type $[M(Me_6[14]aneN_4)Cl_2]^{n+}$, the values of Dq^{xy} are as follows: 1700 cm^{-1} (V^{2+}), 1460 cm^{-1} (Cr^{3+}), 1940 cm^{-1} (Cr^{2+}), ~2410 cm^{-1} (Mn^{3+}), 2220 cm^{-1} (Fe^{2+}), 2450 cm^{-1} (Co^{3+}), and 1470 cm^{-1} (Ni^{2+}). It follows from this series that the values of Dq^{xy} for triply charged cations are greater than for doubly charged cations and are constant (~2450 cm^{-1}) within the limits of experimental error, while the values for M^{2+} increase markedly in the sequence Ni < V–Cr < Fe.

Table 12. Absorption bands and magnetic moments of tetragonal transition metal complexes.

Compound	μ_{eff}, μ_B	Solvent	ν_1	ν_2	ν_3	ν_4	Refs
$[V(Me_6[14]aneN_4)Cl_2]$	3.71	solid	12.5	17.0 sh	22.0	24.5	182
$[V(Me_6[14]aneN_4)Br_2]$	3.86	solid	10.3	16.0	21.0	23.8	182
$[V(Me_6[14]aneN_4)I_2]$	3.74	solid	8.5	15.5sh	20.0	24.4	182
$[V(5,12Me_2[14]aneN_4)Cl_2]$	3.73	solid	12.9	—	19.2 sh	23.8 sh	182
$[Cr([14]aneN_4)Cl_2]Cl$	—	H_2O	17.5 (20)	24.6 (35)	27.4 (41)		183
$[Cr([14]aneN_4)(H_2O)_2](ClO_4)_3$	—	H_2O	19.6 (24)	24.7 (39)	25.6 (38)	28.6 (38)	183
$[Cr(Me_6[14]aneN_4)Cl_2]$	4.80	solid	14.7 sh	19.4	—	—	184
$[Cr(Me_6[14]aneN_4)Br_2]$	4.82	solid	15.0 sh	20.4	—	—	184
$[Cr(5,12Me_2[14]aneN_4)Cl_2]$	4.87	solid	14.3	19.7	—	—	184
$[Cr(5,12Me_2[14]aneN_4)Br_2]$	4.90	solid	15.4	19.6	—	—	184
$[Mn(Me_6[14]aneN_4)Cl_2]PF_6$	4.90	CH_3CN	10.9 (9)	24.1 sh	26.5 sh	—	135, 185
$[Mn(Me_6[14]aneN_4)Br_2]PF_6$	4.90	CH_3CN	11.7 (17)	23.2 sh	27.0 sh	—	135, 185

Remarks: the assignments for the d^3 configuration (V^{2+} and Cr^{3+}) are as follows: ν_1—$^4E_g \leftarrow {}^4B_{1g}$ transition; ν_2—$^4B_{2g} \leftarrow {}^4B_{1g}$ transition; ν_3 and ν_4—transitions to the components of the split $^4T_{1g}$ level (A_{2g} and ^4E_g); the assignments for the d^4 configuration (Cr^{2+} and Mn^{3+}) are as follows: ν_1—$^5A_{1g} \leftarrow {}^5B_{1g}$ transition; ν_2—$^5B_{2g} \leftarrow {}^5B_{1g}$ transition; ν_3—$^5E_g \leftarrow {}^5B_{1g}$ transition.

It is of interest to note that, in contrast to the cobalt(III) complexes, in the macrocyclic rhodium(III) complexes no splitting of the octahedral band is observed even for compounds in which the *trans*-disposition of the axial ligands has been demonstrated[130 186–188].

Apart from the tetragonal complexes, trigonal-bipyramidal vanadium(II) complexes[182] and pseudo-octahedral chromium(III) [183] and ruthenium(III) [189] complexes have also been obtained.

VII. THE MUTUAL INFLUENCE OF THE LIGANDS IN MACROCYCLIC COMPLEXES

In the studies of the tetragonal complexes of iron(II), cobalt(III), and nickel(II) it has been shown that Dq^{xy} for macrocyclic ligands varies as a function of the nature of the axial ligands and conversely that Dq^z for a specific axial ligand depends greatly on the nature of the coordinated macrocyclic compound. Similar findings were also made for natural macrocyclic complexes[190]. This phenomenon reflects the mutual influence of the ligands and, since the axial ligand is in the *cis*-position with respect to the macrocyclic ligand, reflects the *cis*-influence in complexes of this type.

It has been shown for cobalt(III) [83] and nickel(II) [167] complexes that the dependence of the quantities Dq^{xy} and Dq^z on the nature of the ligands and their mutual influence can be represented by the following simple equations:

$$(\text{for } Dq^{xy} \text{ in the cobalt complexes}), \quad (1)$$

$$(\text{for } Dq^{z} \text{ in the cobalt complexes}), \quad (2)$$

$$(\text{for } Dq^{xy} \text{ in the nickel complexes})\dagger, \quad (3)$$

where δ_L, σ_Z, and Δ_L are increments taking into account the nature of the ligand, for which the value of Dq is determined by the equation, and δ_Z, σ_L, and Δ_Z are increments taking into account the nature of the ligand in the *cis*-position with respect to the ligand whose parameter is calculated by the equation.

The spectroscopic parameters of the macrocyclic complexes, calculated from the data in Tables 9 and 11, as well as the increments in Eqns.(1), (2), and (3) are listed in Tables 13, 14, and 15. The constants in these equations were selected on the basis of the most reliable data and are as follows: $Dq^{xy} = 2450$ cm^{-1} for $[Co(Me_6[14]aneN_4)(H_2O)_2]^{3+}$ in Eqn.(1); $Dq^z = 1500$ cm^{-1} for $[Co(Me_2py[14]aneN_4)Cl_2]^+$ in Eqn.(2), and $Dq^{xy} = 1399$ cm^{-1} for $[Ni(Me_6[14]aneN_4)(NCS)_2]$ in Eqn.(3). The graphical relations between Dq_{exp} and Dq_{calc} are presented in Fig.4. All the straight lines have a slope of unity and the correlation coefficients are 0.975, 0.994, and 0.997 for Eqns.(1), (2), and (3) respectively.

The increments σ_L and Δ_L are determined by the structure of the macrocyclic ligands and the donor properties of the nitrogen atom, the nature of which has already been discussed in connection with the consideration of the tetragonal cobalt(III) and nickel(II) complexes. The values of σ_Z reflect the spectroscopic properties of the axial ligands and increase in parallel with the spectrochemical series for these ligands $Br^- < Cl^- < H_2O < OH^- < N_3^- < NCS^- < CH_3CN < CN^-$ in the case of the cobalt(III) ion. The *cis*-influence of the axial ligands is expressed by the parameters δ_Z and Δ_Z and in the case of cobalt the ligands can be arranged in the following sequence in terms of the parameter δ_Z: $CH_3CN < H_2O < CN^- \leq Cl^- < NCS^- < Br^- < N_3^- < OH^-$.

The influence of the axial ligands on Dq^{xy} can be explained as follows. The part of the electron density orbital d_{z^2} associated mainly with the axial ligands is located in the equatorial plane XY and the mutual influence of the ligands can be transmitted via this orbital, because the maximum overlap of the atomic orbitals of the metal with the orbitals of the donor nitrogen atoms occurs in the XY plane. The influence of the macrocyclic ligand on Dq^z, expressed by the parameter σ_L, can be explained by the steric interactions between the alkyl or benzyl substituents in the macroring and the axial ligands, apart from the cause indicated above. This interaction has been observed in the ^1H NMR spectra of a series of macrocyclic complexes[191] and has also been characterised as the *cis*-influence.

The available data are as yet insufficient to construct a relation similar to Eqn.(2) for the Dq^z of the nickel complexes, although it has been shown for a limited number of ligands (Cl^-, Br^-, N_3^-, and NCS^-) [167] that there is a definite relation between the parameters Dq^{xy} and Dq^z, and that the susceptibility of the axial ligands to changes in Dq^{xy} increases in the sequence $Br^-(-0.54) = Cl^-(-0.54) < N_3^-(-0.39) < NCS(-0.33)$ (the slopes of the linear relations between Dq^z and Dq^{xy} are given in brackets).

It follows from the foregoing that Dq^{xy} and Dq^z are not constants and vary as a function of the properties of the ligands in the *cis*-positions. In the presence of various axial

#This equation is not quoted by Martin et al., [167] but follows from the results obtained.

ligands in the macrocyclic complex the situation is complicated still further, because in calculations of the parameters Dq^{xy} and Dq^{z} it is necessary to take into account the mutual influence of the *trans*-ligands as well as the influence of two different axial ligands on the macrocyclic ligand.

Table 13. The parameters Dq^{xy} and the increments in Eqn.(1) for cobalt(III) complexes of the type $[CoLX_2]^{n+}$ (in cm^{-1}).

L	X								δ_L
	CH_3CN	H_2O	CN^-	Cl^-	NCS^-	Br^-	N_3^-	OH^-	
$Me_6[14]dieneN_4$	2780	2800 sh	—	2620 sh	—	2680 sh	—	—	270
$Me_4[14]tetraeneN_4$	2930	2780	—	2710	—	2600	—	—	240
$Me_2[14]1,3dieneN_4$	2790	2740 sh	—	2730	2570	2510	—	—	210
$[14]aneN_4$	—	2710	—	2650	2600	2510	—	2490 sh	180
$2,3Me_2[14]aneN_4$	2710	—	—	2580	—	—	—	—	120
$Me_2py[14]aneN_4$	—	2590	2530	2500	2480	2460	—	2390	70
$Bz_4[16]tetraeneN_4$	—	—	—	2460	2350	2380	2230	—	0
$Me_6[14]aneN_4$	2600	2540	2470	2450	2380	2380 sh	—	2270	0
δ_Z	−80	0	80	90	140	170	250	270	—

Remark: sh = calculated from the shoulder.

Table 14. The parameters Dq^{z} and the increments in Eqn.(2) for cobalt(III) complexes of the type $[CoLX_2]^{n+}$ (in cm^{-1}).

X	L						σ_Z
	Me_2 py [14] ane N_4	Me_4 [14] ane.	$2,3Me_2$[14] $aneN_4$	Me_4 [14] tetra- ene N_4	Me_6[14]dieneN$_4$	Me_2 [14]1,3 .diene N_4	
CN^-	3230	2930	—	—	2910*	—	1680
CH_3CN	—	2220	2270	1990	2100	2090	780
NCS^-	2140	2120	—	—	1990*	2030	550
N_3^-	2060*	—	—	—	1840*	—	520
OH^-	1770	1750	—	—	—	—	300
H_2O	1630	1540	—	1460	1500пл	1580*	130
Cl^-	1590	1430	1380	1350	1340пл	1270	0
Br^-	1340	1320	1270	1180	1120*	1160	−130
σ_L	0	50	100	160	160	220	—

Remark: sh = calculated from the shoulder; *calculated from the value of Dq^{xy} by Eqn.(1).

Table 15. The parameters Dq^{xy} and the increments in Eqn.(3) for nickel complexes of the type $[NiLX_2]$ (in cm^{-1}).

L	X					Δ_L
	Br^-	Cl^-	CH_3COO^-	N_3^-	NCS^-	
$Me_2Ph_2[14]dieneN_4$	—	1540	1510	—	1470	74
$Bz_4[16]tetraeneN_4$	—	—	—	1473	1465	63
$[14]aneN_4$	1487	1480	—	1445	1418	24
$2,3Me_2[14]aneN_4$	1487	1471	—	1426	1414	16
$Me_6[14]aneN_4$	1492	1469	1430	1413	1399	0
$[15]aneN_4$	1283	1242	—	1227	1202	−205
$Bz_4[16]aneN_4$	1140	1130	—	—	1115	−325
$[16]aneN_4$	1128	1116	—	1087	1074	−342
Δ_Z	−66	−59	−36	−17	0	

It follows from Table 12 that the position of the absorption band associated with Dq^{xy} depends on the nature of the axial ligands in the case of vanadium(II), chromium(II), chromium(III), and manganese(III) complexes. In all probability this phenomenon is general for all transition metals.

As shown in the present review, macrocyclic ligands constitute an interesting class of compounds forming complexes with metal ions. The wide variety of the structures of these complexes is determined both by the structure of the macrocyclic ligands and the properties of their donor atoms, on the one hand, and by the characteristics of the electronic structure of the metal ions, on the other.

Apparently, as for alkali and alkali earth metal complexes with macrocyclic polyethers[8], the relative dimensions of the cavity within the macrocyclic ligand and of the transition metal ion play an important role in determining various properties (kinetic, thermodynamic, spectrochemical, electrochemical, etc.) of their complexes. If the size of the macrocyclic ligand is insufficient for it to be coordinated to the metal in a planar conformation, then complexes of a different structure with a bent macrocyclic ligand are formed. Complexes of this type are formed also when a macrocyclic ligand of sufficient size contains bulky substituents in its ring (particularly at the nitrogen atoms) or when an additional bidentate ligand is involved in the coordination.

Complexes with macrocyclic ligands occupying the equatorial plane in the coordination sphere of the metal are subject to marked tetragonal distortion, which gives rise to a unique possibility for the investigation of the influence of various factors on the spectrochemical parameters of the complexes. It has been shown that the parameters obtained reflect the mutual influence of the ligands in these complexes.

From the spectrochemical point of view, macrocyclic compounds are as a rule some of the most powerful ligands for which the values of Dq have been determined and are inferior, as regards field strength, only to ligands of the type of cyanide ions or nitro-groups.

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