

## Studies of Absorption Spectra

### IX. The Spectra of Cobalt(II) Complexes

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The spectra of hexammine and tris(ethylenediamine) cobalt(II) ions were measured taking special precaution against the formation of the highly coloured oxidation products. The mono- and diammine spectra were found by use of Bjerrum's equilibrium data. The spectra of several octahedral cobalt(II) complexes are compared, and the displacements of band maxima discussed. The spectrum of the tetrachloro complex is shown to agree with the crystal field theory if a tetrahedral configuration is assumed. All the cobalt(II) complexes which have been considered here are magnetically normal, *i. e.*  $S = 3/2$  in the ground state. The strong bands are then attributed to transitions  $S = 3/2 \rightarrow 3/2$  while the weak bands originate from transitions  $S = 3/2 \rightarrow 1/2$ . Further the spectra of complexes with two different ligands are discussed and connected with the configuration and existence of geometrical isomers.

The crystal field theory, primarily set forth in the papers of Bethe<sup>1</sup> and van Vleck and his co-workers<sup>2-4</sup> has been successfully applied<sup>5-9</sup> to the spectra of the transition elements. The present paper compares the measured spectra of different cobalt(II) compounds with the theoretical predictions offered by the crystal field theory. Regular octahedral complexes with cubic symmetry such as the hexaquo ion  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$ , the hexammine ion  $[\text{Co}(\text{NH}_3)_6]^{++}$  and the tris(ethylenediamine) ion  $[\text{Co en}_3]^{++}$  are of particular interest.

The two latter complexes were investigated by Roberts and Field<sup>10</sup>. The absorption spectrum they report for  $[\text{Co en}_3]^{++}$  does not lend itself to a closer identification of the absorption bands. Thus it was observed that the steep absorption below 400  $m\mu$  can be reduced much below what is found by Roberts and Field when air oxidation is completely prevented. The operations were carried out in an atmosphere of nitrogen, and the technique used was to dissolve solid  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  in an oxygen free aqueous solution of the amine. Fig. 1 shows the spectra of 0.005  $M$   $\text{CoSO}_4$  in 12  $M$   $\text{NH}_3$  and in 0.5  $M$  en, containing thus the nearly pure hexammine complexes, according to the equilibrium measurements by Bjerrum<sup>11</sup>. It is apparent from the curves that there is practically no absorption in the near ultraviolet.

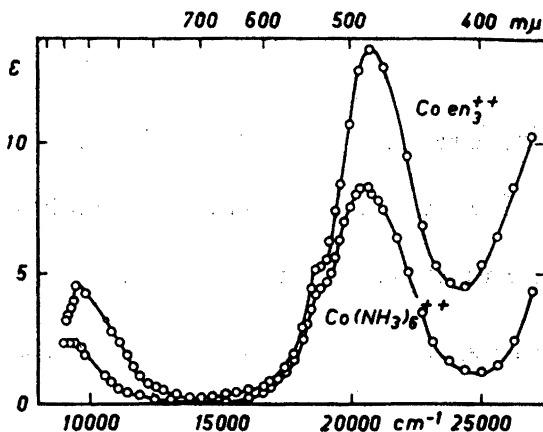


Fig. 1. Absorption spectra of hexaammine and tris(ethylenediamine)cobalt(II) ions. 0.005 M  $\text{CoSO}_4$  (AnalaR) in 12 M  $\text{NH}_3$  and 0.5 M  $\text{en}$ , respectively, at 25° C.

The strongly absorbing oxidation products seem to be one individual compound in each case, since the spectra of the solutions with different degrees of slight oxidation deviate linearly from the spectra of the hexa-complexes. The compounds formed are probably bi-nuclear peroxy complexes which in the course of some hours undergo changes to mono-nuclear cobalt(III) complexes. These latter complexes are known to be much less absorbing than the intermediate peroxy complexes. The reaction mechanism for the oxidation of Co(II) amine complexes is now being investigated in this laboratory.

The method for determining the spectra of the individual nickel(II) ammonia complexes<sup>11</sup> has here been applied to the two first complexes of cobalt(II),  $[\text{Co}(\text{NH}_3)(\text{H}_2\text{O})_5]^{2+}$  and  $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$ , respectively. Fig. 2 gives the two spectra, measured in 2 M  $\text{NH}_4\text{NO}_3$  as well as the spectrum of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  in the same salt solution.

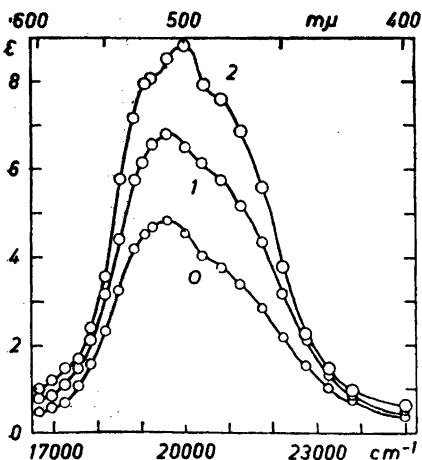


Fig. 2. Resolved absorption spectra of  $\text{Co}(\text{NH}_3)_n^{2+}$  in 2 M  $\text{NH}_4\text{NO}_3$  at  $t = 25^\circ \text{C}$  for  $n = 0, 1$  and 2. Determined from the equilibria constants given by Bjerrum<sup>11</sup> for this salt medium and temperature.

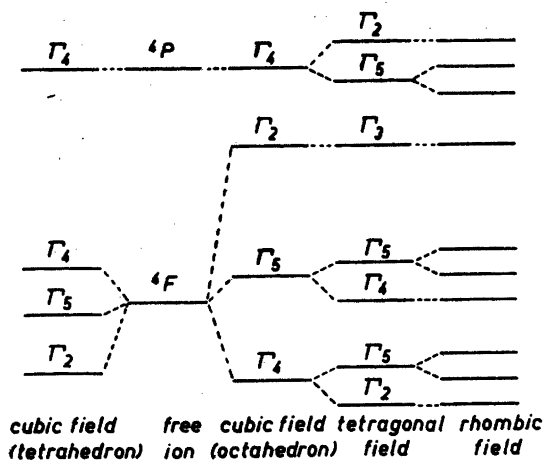


Fig. 3. Energy levels of  ${}^4P$  and  ${}^4F$  ( $d^7$ ) in crystal fields of different symmetry.

The Co(II) ion has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ . Thus two terms with  $S = 3/2$  are possible, *viz.* the ground state  ${}^4F$  and the  ${}^4P$  term which is placed  $15\,400\text{ cm}^{-1}$  above the  ${}^4F$  level<sup>12</sup>. The splittings of these two terms in crystal fields of various symmetry are shown schematically in Fig. 3. The notation is the nomenclature of Bethe<sup>1</sup>.

The orbital degeneracy is

	$\Gamma_1$	$\Gamma_2$	$\Gamma_3$	$\Gamma_4$	$\Gamma_5$
cubic	1	1	2	3	3
tetragonal	1	1	1	1	2

It is seen that a tetragonal field removes nearly all the orbital degeneracy. The effect of a rhombic field is to do away with all the orbital degeneracy.

For Co(II) complexes with cubic symmetry the theory then predicts three bands, originating from transitions between the ground level and the three excited states all with  $S = 3/2$ . Further it is seen that the absorption spectrum for a regular octahedral complex is different from that of a regular tetrahedral Co(II) complex. The crystal symmetry is the same, but the energies of the states are different in the two cases.

An important theorem set forth by Jahn and Teller<sup>13</sup> states that in a stable molecule all orbit degeneracy is removed from the ground state. This rule can be applied to complex ions as follows: Consider a cubic configuration of the ligands around the metal ion. The energy then required to move the ligands a little from their equilibrium positions in the potential holes is of second order in the displacement and therefore small compared to the first

order energy gain produced by a possible accompanying splitting of the ground level. This continues until the ligands have arranged themselves in such a way that the ground state is unable to split up any further; the orbit degeneration of this level is then one. This rule predicts nothing about the order of magnitude of the distortion of the ligands from cubic symmetry, it merely states that there is a distortion. In some cases, however, the effect may perhaps be clearly seen as for example in the complexes of Cu(II). A regular octahedral Cu(II) complex with cubic symmetry has the ground state  $\Gamma_3$ . In a tetragonal field this level will split up into two new states<sup>6</sup>, both once degenerated. The Jahn-Teller rule thus predicts that it is a tetragonal structure which is stable for Cu(II) complexes, as in fact demonstrated<sup>5</sup>.

Fig. 3 shows that if the Jahn-Teller rule is to be obeyed octahedral Co(II) complexes must necessarily be of a tetragonal or of a rhombic structure. That this is the case is strongly supported by magnetic evidence<sup>3</sup>. However, the splittings of the states due to the superimposed rhombic field is only a few hundred  $\text{cm}^{-1}$ , and consequently these splittings only affect the absorption spectra to a very slight extent. It is therefore sufficient to consider the splittings due to the predominant cubic field in order to explain the absorption spectrum. On the other hand it is seen that it is possible to have regular tetrahedral Co(II) complexes, as the ground state here is a cubic  $\Gamma_2$  level which is once degenerated.

#### OCTAHEDRAL Co(II) COMPLEXES

The level order is here  ${}^4F(\Gamma_4)$ ,  ${}^4F(\Gamma_5)$ ,  ${}^4F(\Gamma_2)$  and  ${}^4P(\Gamma_4)$ . The infrared band of  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$  measured by Dreisch and Trommer<sup>14</sup> at  $8\,000\text{ cm}^{-1}$  has been identified<sup>7</sup> as the first transition  ${}^4F(\Gamma_4) \rightarrow {}^4F(\Gamma_5)$ . Similar bands were found for  $[\text{Co}(\text{NH}_3)_6]^{++}$  at  $9\,000\text{ cm}^{-1}$  and for  $[\text{Co en}_3]^{++}$  at  $9\,800\text{ cm}^{-1}$  (Fig. 1).

The theory<sup>9</sup> predicts three bands placed at  $\nu_1 = 4/5 (E_1 - E_2)\text{ cm}^{-1}$ ,  $\nu_2 = 9/5 (E_1 - E_2)\text{ cm}^{-1}$  and  $\nu_3 = 3/5 (E_1 - E_2) + 15\,400\text{ cm}^{-1}$  respectively. The parameter  $(E_1 - E_2)$  is the energy difference between the two possible levels of a single d electron in a crystal field of cubic symmetry.

To obtain the best agreement between the calculated and found absorption maxima we place  $(E_1 - E_2) = 9\,000\text{ cm}^{-1}$  for the aquo-ion,  $(E_1 - E_2) = 10\,500\text{ cm}^{-1}$  for the ammonia complex and  $(E_1 - E_2) = 11\,000\text{ cm}^{-1}$  for the ethylenediamine complex (Table 1). This is in good agreement with the corresponding values for  $(E_1 - E_2)$  in Ni(II) complexes<sup>8</sup>.

The two visible bands in  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$  are then predicted to be situated at  $16\,200\text{ cm}^{-1}$  and  $20\,800\text{ cm}^{-1}$ , as seen in Table 1. The strongest band observed in the spectrum is a double band<sup>15</sup> with the centre of gravity at  $20\,200\text{ cm}^{-1}$ . This band is undoubtedly due to the transition  ${}^4F(\Gamma_4) \rightarrow {}^4P(\Gamma_4)$ , and is split up for similar reasons as the second band<sup>8</sup> of  $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$ . That the origin of this band is due to such a transition is further supported by the splitting found in the mono- and diammine cobalt(II) complexes, which have tetragonal symmetry. The low bands found<sup>7</sup> at  $16\,000\text{ cm}^{-1}$  in  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$  and as shown above at  $18\,500\text{ cm}^{-1}$  in  $[\text{Co}(\text{NH}_3)_6]^{++}$  and  $18\,700\text{ cm}^{-1}$  in  $[\text{Co en}_3]^{++}$  are then identified as  ${}^4F(\Gamma_4) \rightarrow {}^4F(\Gamma_2)$ . The low intensity observed in these bands is probably connected with the fact that the state  ${}^4F(\Gamma_2)$

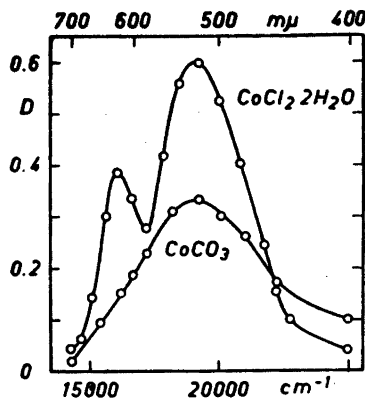


Fig. 4. Reflection spectra of cobalt(II) carbonate and cobalt(II) chloride dihydrate, measured on a Beckman DU spectrophotometer.  $t = 25^\circ \text{C}$ .

has the orbital degeneracy = 1, while the much stronger combining state  ${}^4P(\Gamma_4)$  is three times degenerate.

It may be shown that the symmetry and strength of the crystal field of an octahedral complex can be described in the following way: The sum of the contributions of the two ligands on each axis, we will call respectively  $\sum(x)$ ,  $\sum(y)$  and  $\sum(z)$ . The complex is said to have cubic symmetry when  $\sum(x) = \sum(y) = \sum(z)$ , and tetragonal symmetry when  $\sum(x) = \sum(y) \neq \sum(z)$ . Finally rhombic symmetry occurs when all three functions are different.

The crystal field states are alone determined by the set  $(\sum(x), \sum(y), \sum(z))$ . Thus all the complexes  $\text{MA}_5\text{B}$ ,  $\text{MA}_4\text{B}_2$  have tetragonal symmetry. The lowest possible symmetry, the rhombic, is represented by one of the geometrical isomers of  $\text{MA}_3\text{B}_3$  (and of course in most complexes with three different ligands), while the other isomer of  $\text{MA}_3\text{B}_3$  has cubic symmetry.

The influence on the metal ion of other crystal fields than cubic ones are considered by the authors<sup>5, 6, 8, 17</sup> and by Orgel<sup>16</sup>. It turns out that the monoammine and the *cis*- and *trans*-diammine of  $\text{Co}(\text{II})$  are each expected to exhibit two bands instead of the pure cubic band  ${}^4F(\Gamma_4) \rightarrow {}^4P(\Gamma_4)$ . The band  ${}^4F(\Gamma_4) \rightarrow {}^4F(\Gamma_2)$  cannot be split up by fields of lower symmetry, except when the excited levels of the ground state begin to be populated but this can only account for a few hundred  $\text{cm}^{-1}$  at room temperature. The splitting in *cis*-complexes is generally  $-\frac{1}{2}$  times the corresponding splitting in *trans*-complexes<sup>17</sup>. Thus in most cases the *cis*-complexes have only broad bands, in contrast to the *trans*-complexes where there is a distinct separation into two bands.

Table 1. Comparison of calculated and found absorption maxima for  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$ ,  $[\text{Co}(\text{NH}_3)_6]^{++}$  and  $[\text{Co en}_3]^{++}$  in  $\text{cm}^{-1}$ .

$[\text{Co}(\text{H}_2\text{O})_6]^{++}$	obs.	8 000	$\sim 16\ 000$	20 200
	calc.	7 200	16 200	20 300
$[\text{Co}(\text{NH}_3)_6]^{++}$	obs.	9 000	18 500	21 100
	calc.	8 400	18 900	21 700
$[\text{Co en}_3]^{++}$	obs.	9 800	18 700	21 700
	calc.	8 800	19 800	22 000

The vivid colour changes of certain cobalt(II) salts from red to blue forms may be due to one of two different reasons. Either the bands of the hexaquo ion are only slightly shifted, and can still be recognized, or the configuration of the complex is totally changed with the appropriate consequences for the bands. This difference in spectral change was empirically pointed out by Feitknecht<sup>18</sup> and Katzin and Gebert<sup>19</sup> and rationalized on the basis of crystal fields by Orgel<sup>16</sup>.

The first case, the small changes of octahedral energy levels, is exemplified by many complexes with oxy-anions. Fig. 4 shows the reflection spectrum of cobalt(II) carbonate, measured on the Beckman D.U. The only maximum found is at 530  $m\mu$ , and the usual structure of the band with a shoulder towards blue is still observed. The maximum at 512  $m\mu$  of  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$  is shifted to 540  $m\mu$  in concentrated sulphuric acid.<sup>23</sup> Solutions in phosphoric acid give similar changes especially at elevated temperatures, and Dr. N. Hofman-Bang has kindly pointed out to us that cobalt(II) salts in formamide show reversible changes of colour with temperature. In a spectroscope the blue colour is seen to be due to a broadening of the usual band and a continuous displacement towards the red. Similar observations can be made on solutions of cobalt(II) nitrate in glycerol.

The temperature effects mentioned above are due to shifts of equilibria as the weaker anion and organic solvate complexes are generally formed with absorption of heat. However, the spectrum of a definite complex, *e. g.*  $[\text{Co}(\text{H}_2\text{O})_6]^{++}$  undoubtedly changes with temperature. These changes correspond to stronger crystal fields at lower temperatures resulting in spectral shifts in the same direction as substitution of, *e. g.*, ammonia for water. This hypsochromic effect at low temperature can be demonstrated by pouring liquid air on solid cobalt(II) salts of the usual red colour, which changes to yellow-orange.

Analogous to this effect, the green nickel(II) salts turn sky-blue at liquid air temperature. The observed increased crystal field is probably due to the greater orientation of the ligands at the lower temperature.

#### TETRAHEDRAL Co(II) COMPLEXES

The absorption spectrum of cobalt(II) in concentrated hydrochloric acid has been measured by many authors, *e. g.* Formanek<sup>20</sup>, Jones<sup>21</sup>, Brode<sup>22</sup>, Kiss and Gerendás<sup>23</sup>, Dreisch and Trommer<sup>14</sup> and Katzin<sup>24</sup>. The spectrum as recorded on a Cary spectrophotometer is shown in Fig. 5. If the complex formed was octahedral with two molecules of water, the spectrum would show bathochromic effects and slightly tetragonal splitting, but would otherwise resemble the spectrum of the aquo ion. The purple solid  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  has the environment two water in the *trans*-position and four chloride ions in the plane around the cobalt(II) ion according to X-ray measurements by Vajnstejn<sup>25</sup>. Here the reflection spectrum (Fig. 4) is also seen to resemble other octahedral Co(II) complexes. Contrary to this, the spectrum of a tetrahedral  $\text{CoCl}_4^{--}$  can be described by a cubic crystal field with  $(E_1 - E_2)$  equal to  $-4/9 (E_1 - E_2)$  of an octahedral  $\text{CoCl}_6^{-4}$  with the same distances. The inversion of the levels is indicated by the minus sign, the numerical factor 4/9 is given by one of the

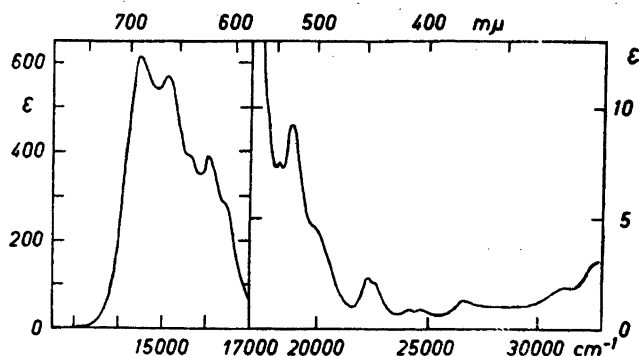


Fig. 5. Absorption spectrum of tetrachloro cobalt(II) ions (0.002 M and 0.05 M  $\text{CoSO}_4$  in 12 M  $\text{HCl}$ ) measured on a Cary spectrophotometer.  $t = 30^\circ \text{C}$ .

authors<sup>6</sup>. Since  $(E_1 - E_2)$  in chloro-complexes is generally smaller than in aquo ions (compare  $\text{Ti(III)}$ ,  $\text{V(III)}$ ,  $\text{Cr(III)}$ ,  $\text{Cu(II)}$ , etc.) one would expect  $(E_2 - E_1)$  to be somewhat smaller than  $4\,400\text{ cm}^{-1}$  in  $\text{CoCl}_4^{--}$ .

The band<sup>15</sup> at  $6\,300\text{ cm}^{-1}$  can be identified as a transition from the ground state  ${}^4F(\Gamma_2)$  to  ${}^4F(\Gamma_4)$  [see Fig. 3], giving  $9/5 (E_2 - E_1) = 6\,300\text{ cm}^{-1}$  or  $(E_2 - E_1) = 3\,500\text{ cm}^{-1}$  in good accordance with the arguments given above. The other internal  ${}^4F$  transition to  $\Gamma_5$  must then be placed far in the infrared at  $\sim 3\,500\text{ cm}^{-1}$ . The very intense band with a complex structure (five or six maxima) between  $14\,300$  and  $16\,400\text{ cm}^{-1}$  is then due to  ${}^4F(\Gamma_2) \rightarrow {}^4P(\Gamma_4)$  transitions which should be placed at  $15\,400 + 6/5 \cdot 3\,500 = 19\,600\text{ cm}^{-1}$ , supporting the idea that  $(E_2 - E_1)$  is even smaller than  $3\,500\text{ cm}^{-1}$ .

Except in the lanthanides and actinides this is the weakest crystal field ever observed. The spectrum must therefore reproduce the atomic energy levels<sup>12</sup> quite exactly. The  ${}^2G$  level which is placed at  $17\,300\text{ cm}^{-1}$  in the free ion has the crystal field splittings<sup>9</sup> in cubic fields amounting to  $+1/5$ ,  $+1/35$ ,  $+1/10$  and  $-13/70 (E_1 - E_2)$ , around the centre of gravity. This corresponds to a total splitting of  $27/70 (E_1 - E_2)$  of the term. In  $\text{CoCl}_4^{--}$  this is below  $1\,500\text{ cm}^{-1}$ . The bands at  $18\,300$  and  $18\,800\text{ cm}^{-1}$  and probably also  $19\,800\text{ cm}^{-1}$  are due to  ${}^2G$ , while the predicted centre of gravity is  $17\,300 + 6/5 (E_2 - E_1) = 21\,500\text{ cm}^{-1}$ . The other weak bands are presumably due to the other doublet levels of  $\text{Co}^{++}$ ,  ${}^2H$ ,  ${}^2F$ ,  ${}^2D$ , etc. They continue down in the ultraviolet (Kiss and Gerendás<sup>23</sup> give the last at  $34\,700\text{ cm}^{-1}$ ) corresponding to the latter doublets which are not known from atomic spectroscopy.

The bands are very narrow which is probably connected with the occurring weak crystal field, just as in the lanthanide and actinide spectra. The splitting of the  ${}^4P(\Gamma_4)$  state is due to  $(L,S)$ -coupling effects, which are also quite large in the free ion<sup>12</sup>. Of the  $(2S+1)(2L+1) = 4 \times 3 = 12$  independent states of  ${}^4P$  the crystal field can only form six different levels, since the Kramers degeneracy cannot be removed. Of these six levels a pure cubic field should furthermore only present four, since two of the levels are four times degenerate on the basis of  $(2S+1)(2L+1)$ . It is highly improb-

able that the fine structure of the weak bands is due only to vibrational states (as in  $\text{MnO}_4^-$  or  $\text{UO}_2^{++}$ ), as postulated by Brode<sup>22</sup> or Yamada and Tsuchida<sup>28</sup> since the intensities are so irregular, and no constant frequency difference can be found with certainty.

The intensity of the bands in  $\text{CoCl}_4^{--}$  is anomalously large, compared with the other cobalt(II) complexes. While the transitions between states with  $S = 3/2$  in most of the complexes have maximal molar extinction coefficients  $\epsilon_n \sim 10$  and the spin-forbidden transitions  $S = 3/2 \rightarrow 1/2$  have  $\epsilon_n \sim 0.1$ , the two different types of bands in  $\text{CoCl}_4^{--}$  have  $\epsilon_n \sim 500$  and 5. This phenomenon is also encountered in chloro- and bromo-complexes of copper(II).

Simple crystal field considerations seem to be able to account reasonably for the experimental evidence, and it is possible to find some indications concerning the configuration of the various cobalt(II) complexes from their spectra. This again depends upon the perturbations from the ligands being strongly dependent on distances. The absorption spectrum of a given complex will then be determined mostly by the ligands in the first sphere, *i. e.*, the nearest environment of the metal ion.

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