

Dedicated to Acad. Prof. Dr. Margareta Giurgea with the occasion of her 90-th anniversary

OPTICAL SPECTRA OF DIVALENT COBALT COMPLEXES

Ath. Trutia*

Bucharest University, Department of Physics, POB MG-11, 077125 Bucharest Magurele, Romania

A study concerning the Crystal Field (Spin-allowed, Spin-forbidden and Charge Transfer) Optical Spectra of the Divalent Co-complexes in different condensed media and site symmetries is presented. A review of our research on the matter, as well as some new results, are analyzed. Symmetry species of the specific complexes and the corresponding Point Groups, as resulted from these spectra are determined. New media, like Poly(EthyleneGlycol) and other related solvents, for the mentioned complexes, have been tested and discussed.

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1. Introduction

Transition-metal ions are good indicators for testing the fundamental behavior of a large series of complexes, involved in a great deal of applications. I'll mention just a few of them: Laser-Active materials, Catalysts, Luminophores, High-tech Fuels and Lubricants, Dyes, etc.

Studies, have been done, for a long time now, among others, on the optical spectra of the divalent Co-complexes, in two of their possible phases (liquid or solid) and two sets of site symmetries: octahedral- and tetrahedral-like. These investigations have been connected with the Crystal Field (spin allowed and spin forbidden), and Charge-Transfer transitions [1-4].

Finite Point Groups formalism [5-8] has been used to interpret the measured data.

Experimentally, all three categories of the mentioned optical transitions have been observed, in all samples, in spite of the fact that for the Centro-symmetric d^n -shell ions complexes the first two kinds of spectra are spatially-forbidden and that some of them are also spin-forbidden. Local imperfections, vibrations, spin-orbit or spin-spin coupling, and wave functions mixing, which have not been taken into consideration when selection rules have been derived, in a first approximation, are the causes for those rules violation. Charge transfer transitions, however, are, in a first approximation, as it is well known, not forbidden by any selection rule.

Let us start with the Crystal Field transitions, i.e., spectra. Usually, Co-complexes belong to two sets of symmetries: Octahedral-like (O_h , D_{4h} , D_{6d} , C_{4v} , C_{3v} , C_{2v} , etc.) and Tetrahedral-like (T_d , C_{3v} , C_{2v} , etc.). Of course, O_h and T_d of these groups (or any other, for that matter) are supposed to be geometrically perfect, but this is almost never the case. There is practically always a static or a dynamic (or both) distortion into their lower subgroups. Out of all these, O_h , D_{4h} and D_{6d} do have a center of symmetry and because of that, their optical, Crystal Field, transitions between the multi-electronic spectral states of the Co-complexes are forbidden by the Spatial Symmetry, Laporte's law. Consequently, the observed spectra should be due to some of the mentioned interactions, capable of mixing symmetrical and unsymmetrical wave functions describing the transition-implied states. That means that the corresponding spectra are rather weak and dependent on defects in the first coordination sphere of the complexes and/or on temperature, through unsymmetrical vibrations. Beside the symmetrical O_h - type subgroups there are also some, like C_{4v} , C_{3v} , C_{2v} , without a center of symmetry. In this case and in all the T_d - like symmetry Co-complexes there is no inversion center, which means that transitions are Laporte-permitted and the corresponding optical spectra are expected to be rather intense (by approx. 80 times, compared to those of the symmetric complexes).

* Corresponding author: Trutia@infim.ro

The degree of a Complex deformation is an important parameter for establishing the group or subgroup it belongs to. The problem is how much deformation is enough to pass to another subgroup. Experimental results are deciding the right, i.e., the active geometry.

The spin selection rule is violated, primarily, by the momenta coupling, as shown later.

The last category of optical spectra of the Co-complexes, the Charge-Transfer ones are, as mentioned before, not submitted to any selection rule, so that they are, at least in principle, very intense and from this point of view, very easy to detect.

Assignment of these categories of optical spectra is favored by the fact that the first ones (Laporte-, spin-allowed), are moderately intense and at low energies; the second (spin-forbidden), are very weak, usually appearing at low temperature, and located at a little higher energies (they can partially mix with those of the first category, though); the third (Charge-Transfer) kind of spectra are located near the limit of the normal, atmospheric, UV-domain, and they are intense, but sometimes obscured by the fundamental absorption band of the host material.

One more point should be emphasized before going into the details of our intervention. No matter the phase of the samples, transition-metal ions are imposing a crystalline order in the first coordination sphere around them. Since the corresponding spectra of these complexes depend solely on this first coordination sphere (except for the eventual fine structure, swallowed by the large bandwidth of the absorption bands), any sample, whether liquid or solid, amorphous or crystallized, should, and are, treated in the frame of the Crystal Field Formalism.

In the limits of this theory, the spectral (multielectronic) terms, of the divalent Co-complexes are derived directly from the corresponding free Co^{2+} terms, shifted and splitted by the electrostatic field of the ligands in the first coordination sphere of the active ion. The most important of these terms (active at room, or lower, temperature) are those derived out of the fundamental unielectronic configuration of the free (spherical) Co-ion, d^7 : 2D , ${}^2(P,D,F,G,H)$ and ${}^4(P,F)$, which are splitted correspondingly by the Crystal Field of lower symmetries [5-6].

2. Liquid phase

Many, different, solvents (Water, Ethanol, Methanol, Acetone, Poly(Ethylene Glycol), etc.), and Co-salts, have been used in the past [2,9,10], and in more recent, investigations [18]. The aim of these studies has been to determine the site symmetries of the Co-ion in these media and the values of the Crystal Field Model's characteristic spectral parameters (D_q , B , C , and λ) especially in connection with the nature of the near-by Cobalt-ligands.

It has been demonstrated [9,10], that the transformation of Co-complexes in acetone (Ac) while stepwisely adding LiCl (the most convenient alkali-halide to be used for furnishing free Cl^- ions) is following a precise mechanism. At the beginning, when no LiCl was added, the Co-complexes show a spectrum which, undoubtedly, can be assigned to a $[\text{CoCl}_2\text{Ac}_2]$ -complex, Fig. 1a. Adding LiCl, due to a higher concentration of Cl^- ions, the $[\text{CoCl}_3\text{Ac}]$ -complexes are formed, Fig. 1b. This process is the only one, as much as the Cl^- ions are concerned: they contribute solely to the formation of the $[\text{CoCl}_3\text{Ac}]$ -complexes until all the $[\text{CoCl}_2\text{Ac}_2]$ -complexes have been transformed into trichloro ones. This process is ending when the molar concentration of the added LiCl is equal with the CoCl_2 concentration. This conclusion is supported by the fact that, during transformation, the corresponding spectra show three isobestic points, as shown in Fig. 1a.

That means that there is no other Co-complexes in the solution except the two mentioned ones. If the process of adding LiCl to these solution is continued, the $[\text{CoCl}_4]^{2-}$ complexes are showing up. Again, there is an isobestic point in the spectra, Fig. 1b, meaning that there are only two Co-species in the solutions: trichloro and tetrachloro Co-complexes. This time, however, the tetrachloro complexes are not completed when the LiCl molar concentration reaches twice the CoCl_2 one, but only at a significantly higher ratio. The process is completed at about $\text{Cl}/\text{Co}=12$, which means that this complex is less stable compared to the trihalo one, but once in shape, it shows, as mentioned before, a clear spectrum, always exactly the same, unaware of it's second coordination sphere, or sample phase.

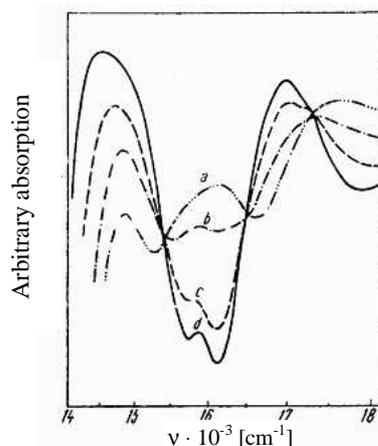


Fig. 1a. Co-complexes transformation, from 2Cl - a, to 3Cl - d.

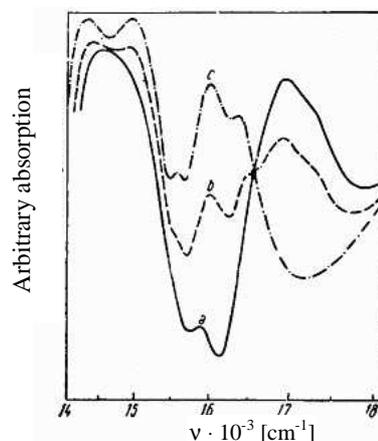


Fig. 1b. Co-complexes transformation, from 3Cl - a, to 4Cl - c.

3. Solid phase

Crystals

One way of studying the Co-complexes in a crystalline phase is to stepwisely vary the concentration of CoCl_2 in different types of crystals. There are two important cases: i) the crystal lattice of the Co-salt mixes with that of the host lattice (like CoCl_2 with CdCl_2), when the sample is a solid solution, or ii) does not mix (like CoCl_2 with KCl), when separate phases of Co-salts are formed inside the host, single- or poly- crystals. A lot of work, very well known by now, has been done in this direction for gathering experimental data and for modeling [1-4, 7], but I'll mention just two very enlightening cases, connected with i) the mechanism of the spin-rule violation and ii) the Charge Transfer model dispute.

i) Spin-exchange interaction

In spite of the fact that the intercombination spectra of the octahedral Co-complexes are twice forbidden, by Laporte's law and by the spin rule, they still appear, especially at low (liquid nitrogen) temperature. There are three sets of transitions of this category, the most intense being the one from ${}^4F({}^4T_g)$ to ${}^2H({}^2T_g)$ at 19.800 cm^{-1} , which has been used in our case. There are two most probable causes for the violation of the spin rule: spin-orbit (S-O) interaction and spin-spin (S-S) coupling of the neighboring metal ions. We have performed investigations to determine which of them is the real one, by dissolving different concentrations of dried CoCl_2 into CdCl_2 single crystals [11]. The samples have been chosen so as to preserve the product cx , of the Co concentration, c , and their thickness x , presuming that the extinction coefficient of the $[\text{CoCl}_6]^{4-}$ complex, ϵ , does not change from one sample to another, which is a reasonable assumption. In these conditions, if the spin rule relaxation is due to a S-O interaction, then the spectra of all these samples should be, overall (spin-allowed and spin forbidden), the same, since this process (S-O coupling) does not depend on the concentration of the active ion. If, on the contrary, the spin-forbidden bands are affected, then the S-S exchange interaction is to be considered for their appearance. The last mechanism is, indeed, the one that does the relaxation and makes the corresponding transitions possible. This is demonstrated by the fact that while for the spin-allowed bands the spectra of all samples are, practically, the same, those forbidden by the spin rule are practically missing under 6% in the low Co-concentration samples, but they do show up in the concentrated ones, as shown in Fig. 2a, for a few concentrations. This is because the most important condition for the S-S coupling is a small distance between the Co-ions, which, of course, is more probable at higher Co-concentrations. This assumption is also based on the fact that these spectra depend on the sample's temperature, indicating a magnetic, i.e., S-S coupling of the neighboring ion's spins, Fig. 2b. The question is, how many Co-ions are coupling their spins to produce the spin-rule violation and what is their form, how do these *clusters* look like. The optical density, E , at 19.800 cm^{-1} , was connected with the active clusters in this respect.

(CdCl_2 crystal is layered. It has sequences of two layers of Chlorine and one of Cobalt. See insert of Table 1 for the arrangement of the Co-ions in the metal layer).

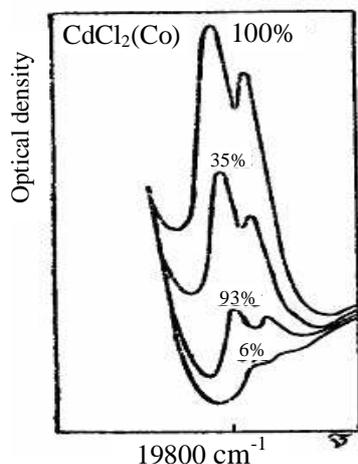


Fig. 2a. Concentration dependence of the Co-clusters.

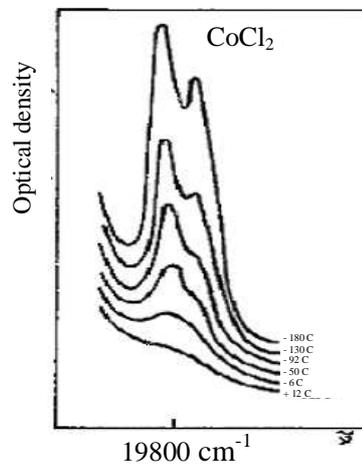


Fig. 2b. Temperature dependence of the Co-clusters.

All the $\text{CdCl}_2:\text{CoCl}_2$ samples have been tested for the real octahedral Co-concentration by comparing their spectra in the solid state and those in water solutions of the previously measured samples, where the six chlorine ions are substituted by six water molecules [11].

Further, we used a statistic to establish the probability of Co^{2+} doublets, triplets, quartets and so on, to octets, called "clusters" taking place for a presumed series of Co-concentrations of 1, 2, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70 and 80 %, in CdCl_2 . Co-Cluster shapes and the used formula are given in Table 1 (the inset is a model of the cluster's Cd environment). Calculation results are given in Table 2 [12]. There is a problem here: only the doublets are unique. As can be seen, each of the other clusters, having the same number of Co-ions, show a few different shapes.

Table 1. Shapes, members and formula for the cluster number calculation.

type	shape		concentration	type	shape		concentration	
singlets	·	1	$c(1-c)^6$	quintets		30	$30c^5(1-c)^{13}$	
doublets	—	6	$6c^2(1-c)^8$			30	$90c^5(1-c)^{14}$	
triplets		9	$27c^3(1-c)^{10}$			60		
		18		$6c^3(1-c)^9$			60	$180c^5(1-c)^{13}$
quartets		12	$108c^4(1-c)^{12}$			60		
		48		$8c^4(1-c)^{12}$			60	
		24		$48c^4(1-c)^{11}$			30	
		24	$12c^4(1-c)^{10}$			60	$90c^5(1-c)^{12}$	
quintets		8				30		
		48				60	$15c^5(1-c)^{12}$	
		12				15		
		15	$375c^5(1-c)^{14}$			30	$30c^5(1-c)^{11}$	
		60					30	
		30					30	
		60					30	
		30					30	
		60					30	

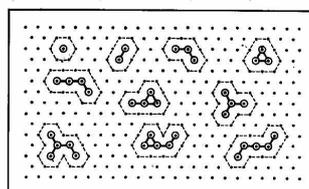


Table 2. Cluster proportions of Co-ions in a CdCl₂ lattice.

cluster type	c (mol%)								
	1	2	5	10	15	20	25	30	40
singlets • $c(1-c)^6$	0.94148	1.77168	3.67546	5.31441	5.65724	5.24288	4.44946	3.52947	1.86624
doublets -- $6c^2(1-c)^8$	0.05536	0.20418	0.99513	2.58280	3.67862	4.02653	3.75423	3.11299	1.61243
triplets --- $27c^3(1-c)^{10}$	0.00244	0.01765	0.20207	0.94143	1.79402	2.31928	2.37573	2.05924	1.04486
Δ $6c^3(1-c)^9$	0.00055	0.00400	0.04727	0.23245	0.46902	0.64425	0.70392	0.65373	0.38698
quartets --- $108c^4(1-c)^{12}$	0.00010	0.00136	0.03647	0.30502	0.77771	1.18747	1.33635	1.21084	0.60184
Y $8c^4(1-c)^{12}$	0.00001	0.00010	0.00270	0.02259	0.05761	0.08796	0.09899	0.08969	0.04458
△ $48c^4(1-c)^{11}$	0.00004	0.00061	0.01706	0.15063	0.40664	0.65971	0.79191	0.76878	0.44581
◇ $12c^4(1-c)^{10}$	0.00001	0.00016	0.00449	0.04184	0.11960	0.20616	0.26397	0.27457	0.18575

The next step was to compare the simulated results with those of the experimental ones. This was done by a graphic representation of the total Co-concentrations, c , in O_h positions, against cluster-concentrations, c_c , for simulated and real clusters. The result is given in Fig. 3. As can be seen, the real cluster, responsible for the S-S relaxation of the spin rule can not be the doublets (as they are, in many cases, concerning especially magnetic behavior of such, diluted, samples). Also, it is hard to believe that it could be due to a higher cluster than triplets. So, the most probable cluster implied in the process seems to be made out of three Co-ions, as indicated by the low concentration samples, but it does not correctly respond for higher Co-concentration ones. Another difficulty consists in the fact that there are several types of triplet clusters: two of them are opened, C_3^o , and one is closed, C_3^c . Furthermore, the triplets are also parts of the other, higher-order clusters. For short, if we add all closed triplets and put the results on the mentioned graphic, a good result is obtained, Fig. 4 (and it is not the opened triplets). This is telling us that the clusters responsible for the spin rule violation are, in this case, all the closed Co-triplets, C_{3a}^c .

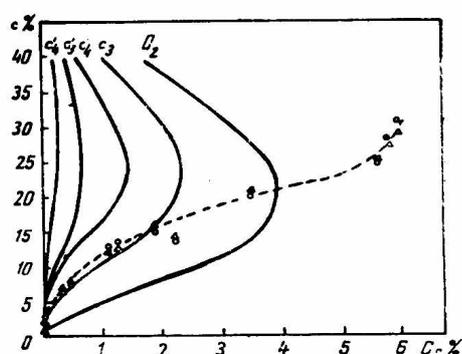


Fig. 3. Cluster concentration:
Calculated —; experim. ---

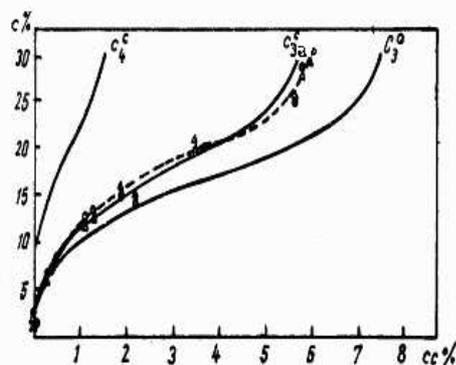


Fig. 4. Cluster fitting: experimental
to all closed triplets, C_{3a}^c .

ii) Charge Transfer Spectra

Another disputed aspect of the Co-complexes optical spectra where we have been implied, concerns the Charge Transfer phenomenon. In the literature [13-14] the spectrum of the KCl:CoCl₂

turbid crystal has been interpreted as belonging to a new-model Co-complex, namely to an interstitial Co-ion in the KCl lattice, in spite of the fact that the Crystal Field spectra of these (turbid) samples were exactly the same with those of the well known "normal", tetrahedral Co-complexes. Because of this, the new model should not be possible since in such an interstitial position the Co-ion should "feel" a rather weaker influence from its neighbors (compared to that in a "normal", T_d , Co-complex, to say nothing of the four K^+ -ions in the first coordination sphere) which should certainly shift the Crystal Field spectra towards lower energies. Experimentally, this is not the case: the spectra are in the same position as for the "normal", T_d , Co-complexes.

The first observation to be considered here is that the crystalline structure of KCl and $CoCl_2$ are different. So, when melt together, they do not mix. This is evident, with no other test, by the fact that these crystals are always turbid. That means that Co ions are building their specific double salt lattices.

Two stable Co-Cl combinations, indicated by their eutectic ratios, are expected to be formed in a KCl: $CoCl_2$ samples [15], Fig. 5. At around molar 33.33%, $CoCl_2/KCl$ there is K_2CoCl_4 , having a clear "normal" tetrahedral structure, then, at approx. 50%, $KCoCl_3$, with a perovskite, octahedral symmetry Co-complexes are formed.

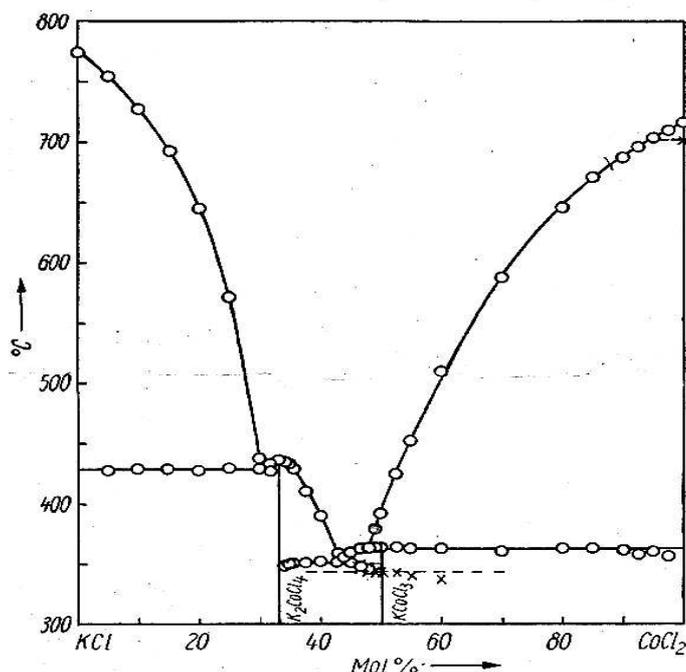


Fig. 5. Eutectic components of $CoCl_2$ in KCl.

We have grown, by Bridgman method, KCl single crystals, with different concentrations of $CoCl_2$, added to the melt [16]. These crystals are always turbid and, depending on the $CoCl_2$ quantity, and on the crystal growing speed, separate phases, made of just mentioned Co-salts are building up, easily seen under a microscope, Fig. 6. These phases have, more or less, the same dimensions and shape, independent on the Co-concentration, but their number depends on the initial Co-concentration and crystal-growing speed. In fact, if the growing speed is very low, segregation effect is preventing almost entirely the Co-ion to form separate phases in KCl, but when they do, these Co-structures have a normal tetrahedral Co-complexes, their Crystal Field spectra are normal and the Charge Transfer spectra are belonging to the usual T_d Co-complexes, no need for a new, interstitial model.

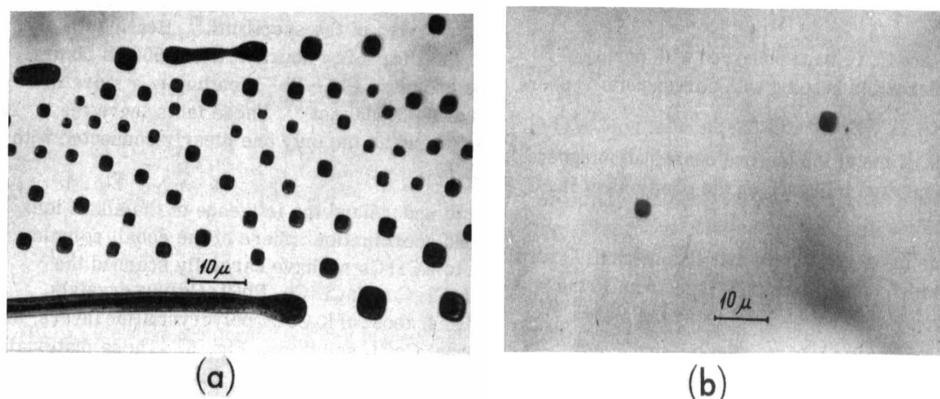


Fig. 6. K_2CoCl_4 islands in KCl lattice at high (a) and low (b) Co-concentration.

These experiments have been repeated by using other alkali-halide host lattices: LiCl, NaCl, and RbCl. All their spectra are given in Fig. 7. A correspondence has been established between the first excitation energy of the alkali-metal and the Charge Transfer energy [16]: their consecutive energy differences are the same. This led us to the conclusion that the first excitation energy of the alkali-ions and the charge transfer energy are connected, Table 3. On these results a tentative model has been proposed for the energy levels implied in the Charge Transfer measured spectra, of the K_2CoCl_4 complex in a KCl/ $CoCl_2$ system, Fig. 8.

Table 3. Energies and peak positions are given in eV.

Element	$E_{excit.}$	$\Delta E_{excit.}$	C.T. Peaks	ΔE_{peaks}
Li	1.84	-0.27	5.47	-0.26
Na	2.11	0.49	5.73	0.49
K	1.62	0.04	5.24	0.04
Rb	1.58		5.20	

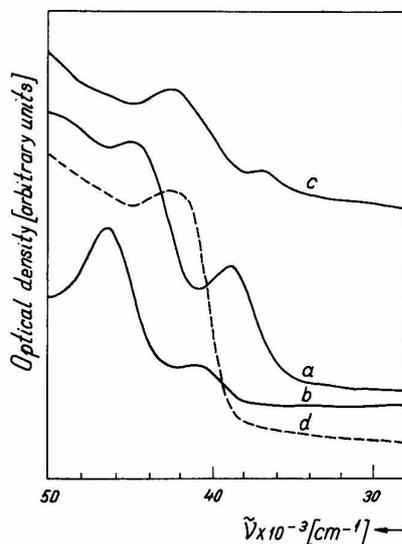


Fig. 7. Charge Transfer spectra of $CoCl_2$ in LiCl -a, NaCl -b, KCl -c, RbCl -d.

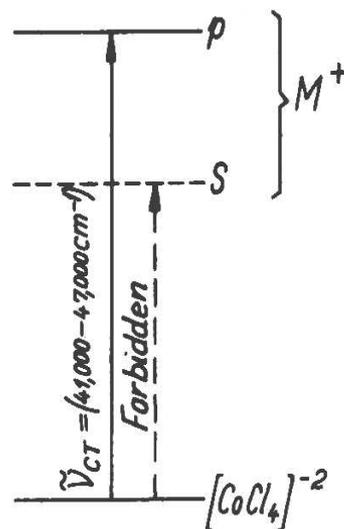


Fig. 8. Proposed Charge transfer optical transitions.

It is important to notice that these Co-complexes in PEG, contrary to what happens in Acetone, do not need addition of LiCl for supplying the free Cl⁻ ions for building the tri or tetra chloro Co-complexes.

So, the problem here is where the Chlorine ions (necessary to build up the trichloro and tetrachloro Co-complexes) are coming from? There are quite a few papers concerning the optical spectra of these Co-complexes [18-23]. Their interpretation, however, are not quite satisfactory. The main problem is the fact that six oxygens from inside-the-chain are, sometimes, believed to form pure octahedral Co-complexes, thus providing free chlorine ions necessary to build the tetrahedral-like higher chloro Co-complexes. Of course, this may be, sometimes, the case, but another possibility of playing the role of ligands for the octahedral Co-species is the O atom from an OH-group at the end of the PEG molecules. Then, there is a problem with using methanol as an intermediate solvent for the CoCl₂/solidPEG systems. It is believed [18] that the alcohol evaporates once it has played its role of dissolving the Co-salt in PEG. This assumption is, however, not well established, or at least it is not for the CoCl₂/PEG, as we try to demonstrate.

Our experiments concerning the optical absorption spectra of the liquid PEGs (amv=200 to 600) at room temperature, show almost pure [CoCl₃O]⁻ complexes. Those of the solid PEGs with methanol are, clearly showing [CoCl₄]²⁻ complexes, while if CoCl₂ is directly dissolved in a solid PEG by heating the salt-oligomer mixture, [CoCl₃O]⁻ complexes are obtained, like for the liquid PEGs.

We have tried to gather some more information concerning the above mentioned problems by looking for other solvents, besides Acetone and PEG, with either no available oxygen inside the molecule, other than OH (Mono(Ethylen Glycol), Propylene Glycol, Ethanol, Methanol), or no OH-groups in their composition (Acetaldehyde, Diethyl Ether, Formaldehyde, Tetrahydrofuran). Di(Ethylene Glycol), DEG, and Tri(Ethylene Glycol), TEG, having both kinds of O atoms like any PEG, were also tried.

The spectra of the pure CoCl₂/Acetone solutions (no LiCl added) indicate, as mentioned before, the presence of the [CoCl₂O₂] complexes and not those of the [CoCl₃O]⁻ or [CoCl₄]²⁻ ones. Our recorded spectra of the CoCl₂/MEG samples contain solely the absorption band of the O_h complexes having OH-ligands (no tetrahedral Co-complexes, except for very high concentration of Cobalt) and so do all the OH-only solvents, while the CoCl₂/DEG samples do, primarily, show the bands of the [CoCl₃O]⁻ complex, like the other O-only solvents, or liquid PEGs. Moreover, raising the temperature (to around 100 °C) of a solid PEG [CoCl₃O]⁻ complex, shows a tendency to change its spectrum to that of the [CoCl₂O₂] complex. There are other changes of the spectra with increasing sample's temperature, especially those belonging to the OH containing molecules, where tetrachloro Co-complexes are favored.

5. Conclusions

As a conclusion, based on all these experimental facts, we propose the following picture for what, we believe, is happening with the Co-complexes in some of the mentioned cases.

1. CoCl₂ is not easily dissociated in Acetone: no OH in it. To build tri or tetra chloro Co-complexes, Chlorine ions must come from outside (addition of LiCl). In CoCl₂/PEG, acting alone (no methanol, or LiCl added), however, a relatively moderate quantity of O_h Co-complexes are produced, with the OH ends of the PEG as ligands, providing, by this process, the necessary free Cl⁻ ions for building, especially the trichloro Co-species. This process is easier to take place in the low amw PEGs (there are more OH groups in a given volume), while high amw PEGs need alcohol to do the job. Since the spectra of all tetrahedral-like Co-complexes are about 80 times more intense compared to those of the O_h ones, even a small quantity of T_d Co-complexes is enough to produce the corresponding intense spectra.

2. The above interpretation is in agreement with the mentioned results [8-9] concerning formation of the trichloro and the tetrachloro Co-complexes in CoCl₂/Acetone, when a free Cl⁻ ion producer, LiCl, is present: first, all dichloro complexes have to become trichloro, before the tetrachloro ones can start building up. It looks like the trichloro are more easily to produce and more stable. In fact we may say that in the process, as many chlorine ions are produced as needed to make the dichloro Co-complexes to become trichloro. Then the Chlorine concentration has to grow much more before the tetrachloro Co-complexes are the only ones in the samples, i. e., they are less stable compared to the trichloro ones. All these are also valid for PEGs. The reason the tetrachloro seem

to be more stable in the PEG/Alcohol solvents is the high OH concentration there, i.e., higher free Cl⁻ ion concentration. Therefore, the spectra of the CoCl₂/PEG-Alcohol samples are, from the beginning, tetrachloro, T_d, spectra and do not show the intermediate case of trichloro species.

3. The in-the-chain oxygen atoms of PEG can have an important role favoring, as a fourth ligand, the trichloro, i.e., the [CoCl₃O]⁻ complexes (having a C_{3v}-symmetry). The same role can have the unique O atom in Acetone, but not in a solvent without a -C-O-C-, or C=O group, nor in a solvent having OH group only, since these oxygen atoms are more suitable and too busy to form O_h Co-complexes.

4. Temperature dependent spectra should thoroughly be investigated and analyzed. They may bring important information on the intimate structure of the mentioned T_d Co-complexes.

References

- [1] D. S. McClure, *Solid State Physics* **9**, 399 (1959).
- [2] C. K. Jorgensen, *Adv. Chem. Phys.* **5**, 33 (1963).
- [3] J. Ferguson, D. L. Wood, K. Knox, **39**, 881 (1963).
- [4] A. Bohun, *Ath. Trutia, Phys. Stat. Sol.* **9**, K 131 (1965).
- [5] H. A. Bethe, *Ann. Physyk*, **3**, 133 (1929).
- [6] Y. Tanabe, S. Sugano, *J. Phys. Soc. Jpn.* **9**, 753 (1954).
- [7] A. Beri, T. P. Das, *Ath. Trutia, V. Gheordanescu, Rom. Rep. Phys.* **46**, 9 (1994).
- [8] *Ath. Trutia, J. Optoelectron. Adv. Mater.* **6**(4), 1331 (2004).
- [9] D. Fine, *J. Amer. Chem. Soc.* **84**, 1139 (1962).
- [10] *Ath. Trutia, M. Musa, Rev. Roum. Chem.* **11**(8), 927 (1966).
- [11] *Ath. Trutia, F. Iova, M. Voda, Rev. Roum. Phys.* **26**, 1021 (1981).
- [12] *Ath. Trutia, F. Iova, M. Voda, Phys. Stat. Sol. (b)*, **84**, 817 (1977).
- [13] A. Mehra, *Jap. J. Appl. Phys.* **6**, 1030 (1967).
- [14] S. Washimiya, *J. Phys. Soc. Jpn.* **18**, 1719 (1969).
- [15] H. J. Seifert, *Z. Anorg. Allg. Chemie* **307**, 137 (1961).
- [16] *Ath. Trutia, M. Voda, J. Chem. Phys.* **64**, 2715 (1976).
- [17] *Ath. Trutia, M. Voda, A. Vasile, Rev. Roum. Phys.* **12**, 101 (1967).
- [18] M. S. Mendolia, G. C. Farrington, *Electrochim. Acta*, **37**, 1695 (1992).
- [19] G. Stanescu, *Ath. Trutia, J. Optoelectron. Adv. Mater.* **7**(2), 1009 (2005).
- [20] J. McBreen, X. Q. Yang, H. S. Lee, Y. Okamoto, *Electrochim. Acta* **40**, 2115 (1995).
- [21] C. A. Furtado, A. O. Porto, G. G. Silva, R. A. Silva, M. A. Pimenta, M. C. Martins-Alves, P. J. Schilling, *J. Polym. Sci. Part B: Polym. Phys.* **39**, 2572 (2001).
- [22] R. A. Silva, G. G. Goulart, M. A. Pimenta, *Electrochim. Acta* **46**, 1687 (2001).
- [23] G. Stanescu, *Ath. Trutia, Proc. SPIE* **5581**, 728 (2004).