Chiral Cr(III) complexes as promising candidates for Circularly Polarized Luminescence

Author(s), Maxime Poncet,[a] Juan-Ramón Jiménez,\*[a],[b] Amina Benchohra[a] and Claude Piguet\*[a]

[a] M. Sc. Maxime Poncet, Dr Amina Benchohra, Prof. D. Claude Piguet. Department of Inorganic and Analytical Chemistry, University of Geneva, quai E. Ansermet 30, CH-1211 Geneva 4, Switzerland. E-mail: Claude.Piguet@unige.ch

[b] Dr Juan-Ramón Jiménez, Department of Inorganic Chemistry University of Granada, Unidad de Excelencia en Química (UEQ) Avda. Fuentenueva S/N, 18071, Granada, Spain. E-mail: Juan.JimenezGallego@unige.ch;

Abstract: Seeking for chiral chromophores with efficient Circularly Polarized Emission (CPL) is one of the on-going hottopic in the scientific community due to their potential applications in emerging fields such as spintronics and photonics. Beyond the largely exploited p-block, precious 4d/5d-block and f-block chiral complexes, the chiral 3d-block Cr(III) complexes have recently raised the interest of chemists because of its crust earth-abundancy, its kinetic inertness and the promising metal centered Cr(2E) and Cr(2T1) spin-flip transitions. These transitions could provide large dissymmetric factor (*g*lum), in a chiral environment, and high luminescence quantum yields when six-membered strong field chelate rings coordinate to Cr(III). The concomitant increase in both parameters has been established as essential for applications. In this mini-review we intend to focus our attention on the state-of -the art for the design of pseudo-octahedral chiral mononuclear Cr(III) complexes together with the associated chiroptical characteristics. The promising electronic properties of these complexes together with their low cost make these underexplored systems appealing candidates for CPL applications.

1. Introduction

The phenomenon of Circularly Polarized Luminescence (CPL), which is the emission of polarized light with a certain degree of handedness from a chiral luminophore, has attracted the chemists and physicists since in 1948 Samoilov observed this phenomenon in a sodium uranyl acetate crystal.[1] Later on, Oosterhof and Emeis reported for the first time the CPL measurements in solutions for the organic molecule trans-β-hydrindanone and for a coordination complex [Cr(en)3]3+ where en stands for ethylenediamine.[2] Currently, the research devoted to CPL arises by the need for chiroptical features in a wide range of applications which spans from technological application (security inks, CP-OLED, etc)[3] to biological applications (molecular probes, bioimaging, chiral recognition, etc)[4] and it is related to the concomitant development of CPL spectrophotometers and their growing availability in the market.

Major activity in the field of CPL is currently focused on the development of chiral chromophores such as: organic dyes,[5] 4d and 5d metal complexes,[5a, 5b] lanthanides-based complexes[6] or more sophisticated supramolecular architectures.[7] The latter approach seems to be a novel strategy to enhance the glum in organic systems.[8] Highly efficient CPL emitters requires large dissymmetry factors (glum) and high quantum yields (*φ*).[5c] The first parameter amounts to the degree of “enantiorichness” of the CP light emitted from a chiral chromophore and it can, theoretically, reach values of -2 or 2 when either pure right- or left-handed polarized light is emitted after standard excitation, and the second one states for the ratio photon absorbed/emitted and should be also maximized. As it has been previously demonstrated, chiral organic chromophores as well as 4d and 5d metal complexes are not good candidates for enhancing the dissymmetry factors due to the electric-dipole allowed character of their electronic transitions.[6b] However, they usually show high *φ* arising from Metal-to-Ligand Charge Transfer or Ligand-to-metal Charge transfer and π\* → π transitions, which can compensate somehow their low glum. In addition, their kinetic inertness and low cost, in the case of organic molecules, make those systems still good candidates for applications.

On this basis, enhancement of glum by a chiral molecule requires the operation of electrically forbidden and magnetically allowed electronic transitions (vide infra). That is, the intrashell f-f and d-d transitions.[9] The success of lanthanide systems can be assessed in Cs[Eu[(+)-(hfbc)4] (hfbc = (+)-3-heptafluorobutylyryl-camphorato) which displays a record value of glum = +1.38 at 595 nm in solution at room temperature.[10] However, the high cost due to their extraction and purification together with their intrinsic kinetic lability are not negligible shortcomings for applications. Currently, the research of photoactive molecules based on earth-abundant metals (basically first-row d-block metals) is an emerging area because they represent a realistic alternative to precious metals (Ru, Ir, Pt or Au) and lanthanides within the context of energy conversion.[11] However, the lack of emissive states in 3d metal based complexes due to their limited ligand field strength have restricted their use in the field of photochemistry although much efforts are being devoted to overcome this.[12] Together with the development of those cheap photoactive molecules, we and others started to exploit the intrinsic nature of the d-d transitions in the context of CPL. Since the development of the ruby laser by Maiman,[13] Cr(III) complexes are among the most investigated coordination complexes in photophysics. Because of their inertness due to the large crystal field stabilization energy (d3 electronic configuration)[14] and their NIR Laporte and spin forbidden Cr(2E→4A2) and Cr(2T1→4A2) emissions when embedded under a strong ligand field environment,[13-14, 15] these metal complexes open new ways for the development of CPL emitters based on cheap metals.[16]

This mini-review reports on the examples of chiral Cr(III) reported up to date together with their chiroptical properties.

2. Chirality in Cr(III) complexes

General chirality definition relates to the geometric property of an object of not being superimposable on its mirror image. The genesis of chirality drew on the outstanding development of stereochemistry, energized by Le Bel [17] and van’t Hoff [18] in the organic field and extended in the inorganic one by Werner,[19] at the end of the 19th century. However, it was not until a century later, in 1966, that its formalization was established by Cahn, Ingold and Prelog (CIP).[20] The renowned trio defined a clear-cut classification structure accounting for the several chirality types, notably those that did not originate from a tetrahedral carbon. Thus, the CIP rules are now basis of use to determine molecules configuration and describe the possible chirality encountered in organic chemistry and coordination chemistry, *i.e*. central chirality, planar chirality, helical chirality and axial chirality. Admittedly, the understanding of the stereochemistry deviating from organic systems harboured greater complexity (than carbon’s one) and was thus deferred. Nevertheless, the d-block is an undeniable source of compounds featuring multi-faceted chirality. Chiral mononuclear Cr(III) examples reported noticeably demonstrate it, with chirality essentially induced by the wrapping of chelates around the metal center (helicity), chiral ligands (R/S), or by the ligand conformation within individual rings (δ/λ).

Prior to analyze these systems, it may be convenient to specify chirality from a symmetry-oriented perspective. To be chiral, a molecule must have a symmetry devoid of improper symmetry operations (*i.e*. inversion center, reflective planes, rotation-reflection axes). Interestingly, chirality was originally termed *dissymmetry* by Pasteur who remarkably suspected the crystal dissymmetry as a result of a dissymmetry at the molecular level.[21] It is also worth noting that it should not be confused with *asymmetry*-referring to the absence of symmetry elements (except the identity E). To observe this rule experimentally and access chiral complexes, chemists can adapt their design tuning ligands denticity, flexibility, symmetry as well as their coordination mode. A general description of these points will be outlined using Cr(III) compounds based on: *(i)* achiral planar ligands, *(ii)* stereogenic ligands and *(iii)* achiral flexible ligands inducing chirality upon complexation. Illustrations of case *(i)* are treated according to the ligands denticity, up to three. Readers interested in further details are referred to corresponding literature.[22]

2.1. Helical chirality

Monodentate ligands (η1). First, the arrangement of six monodentate ligands A around the metal leads to the highest accessible symmetry Oh, which is achiral. The successive replacements of A by a different ligand B exclusively lead to the formation of achiral compounds with reduced-symmetry. The heteroleptic complexes [MA4B2] and [MA3B3] have both two geometrical isomers, cis/trans in the former case and facial (*fac*) and meridional (*mer*) for the latter. It is only the distribution of at least three different monodentate about the metal center that enables the emergence of chirality, of central kind. However, examples of this type are limited, likely due to synthetic challenges.

Didentate ligands (η2). On their side, didentate chelates are one of the most often encountered sources of chirality in coordination chemistry. Bis and tris-(chelate) complexes display a helicity (Δ or Λ) associated to the trigonal twist of the ligands. The highest chiral symmetry D3 is attained with homoleptic complexes [M(η2-A)3], based on planar ligands (such as the archetypal bipyridine, phenantroline or oxalato ligands) (Figure AB1). Examples range from mononuclear to sophisticated supramolecular architectures [ref]. The number of geometrical isomers increase with unsymmetrical ligands as [M(η2-AA’)3] can exist as C3-symmetrical *fac*-isomer or C1-symmetrical *mer*-isomer. Naturally, similar situation arises in the case of heteroleptic complexes [M(η2-A)2B2] with two geometrical isomers possible. The *cis*-[M(η2-A)2B2] isomer of C2-symmetry is chiral, as its counterpart [M(η2-A)2(η2-B)2], while the *trans*-[M(η2-A)2B2] isomer of D2*h*-symmetry is achiral.

Tridendate ligands (η3). Contrary to didentate ligands, tridendate planar ligands provide fewer opportunities to achieve chiral complexes. For instance, homoleptic complexes [M(η3-A)2] are achiral, whether it be in a *fac* or *mer*- coordination mode. Important examples are the emblematic D*2d*-symmetrical bis(terpyridine) chromium(III) [Cr(tpy)2] [23] and the S6-symmetrical [Cr(tpe)]3+.[24] The situation is the same for the *fac-* (C3*v*) and mer-(C2*v*) heteroleptic complexes [M(η3-A)(η3-B)], which are achiral. In this study case, chirality can emerge from the arrangement of unsymmetrical planar ligands around the metal ion, leading for instance to *fac* or *mer* tris(chelate) species [M(η3-A2A’)2], both of C2-symmetry. However, to our knowledge there are no such examples reported with Cr(III). Finally, non-planar multidendate ligands can enable complexes gaining dissymmetry, as discussed section 2.3.

2.2. Chirality brought by chiral ligands

To circumvent non-chiral symmetries, a natural strategy consisted in connecting inherent chiral ligands to the metal center. In this way, several stereogenic derivatives as the *R/S*-1,2-diaminopropane (*R/S*-pn) served for the synthesis of optically active complex such as [Cr(CN)4(*R/S*-pn)] compounds,[25] derived from the C2*v*-symmetrical achiral form [M(η2-A)B4]. The central chirality of organic compounds was also combined to the complexes helical chirality resulting in pairs of diastereomers, often with the added benefit of diastereoselective self-sorting or possible use of conventional chromatography techniques. For instance, Benedetti *et al.* investigated chirality transfer in a series of tris-chelates Cr(III) complexes based on dithiophosphates.[26] Starting from enantiopure (+)-(S)(S)-Mebdtp, they evidenced the diastereoselective formation of the complex Λ-(-)-[Cr(+)-(S)(S)-Mebdtp] in solution while those of Δ-(-)-[Cr(+)-(S)(S)-Mebdtp] in solid state. Diastereoisomeric crystallization was also early exploited with amino-acids and kinetically inert transition metals.[27]

2.3. Chirality arising from chelate rings conformation

The third strategy advancing over the past years in the design of chiral Cr(III) complexes, relies on flexible chelate ligands. Non-planar ligands can undergo a conformational twist upon complexation (Figure AB2). This deviation from planarity within individual ring give rise to δ/λ ligand conformations. A striking

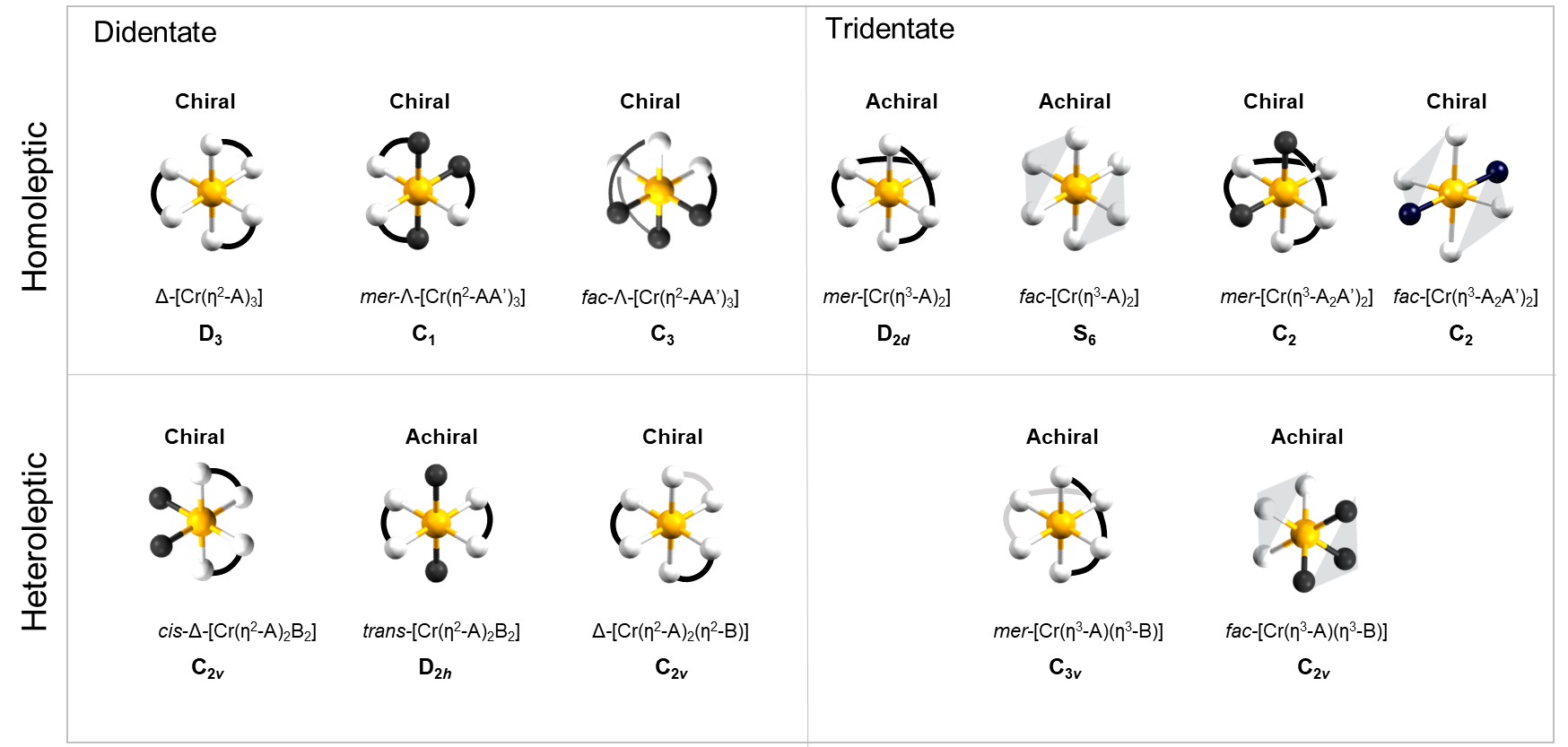


Figure 1. Schematic representation of homoleptic and heteroleptic tris(didentate) and bis(tridentate)complexes and their corresponding symmetries.

example of this is given by the bis(trichelate) [Cr(dqp)2] and [Cr(ddpd)2] (where ddpd (N,N’-dimethyl-N,N’-dipyridine-2-yl-pyridine-2,6-diamine)[28] and dqp (2,6-di(quinolin-8-yl)pyridine)[16a]) displaying a helical structure formed by the ligand twist. Two kinds of stereodescriptors can be assigned to these complexes: *(i)* *P*/*M* descriptors accounting for the helical chirality of the whole structure, where a right-hand helix will be defined as *P* (plus) and the other way around for *M* (minus). *(ii)* δ/λ are associated to the stereochemistry of the individual chelate ring, δ for right-handed twisted ligands and λ for the opposite. Interestingly, meso isomers were not observed due to their higher energy conformation [29]. Heinze *et al* found by TD-DFT, an energy barrier of racemization in [Cr(ddpd)2]3+ of 215 kJ/mol, strengthening the unlikelihood of the process.[16b] Concerning didentates, although ethylenediamine (en) was one of the most used ligand in the early Cr(III) coordination chemistry, the existence of these conformational twists was little referenced or mentioned. Nevertheless, some reports on tris-ethylenediamine complexes demonstrated Λ-[M(δ-en)3]n+ and Δ-[M(λ-en)3]n+ were favored diastereomers in crystalline state.[30]

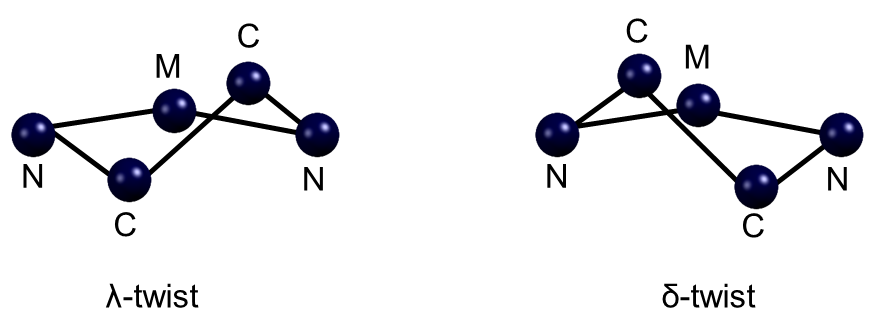


Figure 2. Chiral conformational twists of a five-membered flexible chelate ligand.

3. Circular Dichroism (CD) and Circularly Polarized Luminescence (CPL)

Among the different chiroptical properties, circular dichroism (CD), which is the asymmetric absorption of CPL by a optically active molecule, is one of the most used technique to empirically assign the structure of, for example, small molecules or secondary structure of proteins.. The CD spectra is recorded as the difference in absorption of one circularly polarized light compared to the other, given as Δε, in function of the wavelength. When the value of Δε goes from negative to positive, the effect is called positive Cotton Effect after its discoverer[31] and vice-versa for the opposite.

CD is a technique that must be handle with care when comparing results as the observed effect is temperature, solvent and concentration dependant.[32] Furthermore, if the two spectra recorded are mirror images of each other, it does not necessarily mean that each sample is enantiopure. Therefore, prior good chiral resolution is required. As enantiomers have the same physico-chemical properties in a achiral medium, , separation of the racemate is a challenge. Cation-exchange chromatography using a chiral support,[33] Capillary Electrophoresis,[34] selective crystallisation using chiral counter ions[35], chiral stationary phase HPLC[16b, 29] and supercritical fluid chromatography[36] are different techniques that have been proven to be efficient in the separation of inorganic complexes.

Contrary to the CD experiment where the sample is excited with a circularly polarized (CP) light source, in a CPL measurement, the sample is irradiated with non-polarized light in a region where the photons can be absorbed. Spontaneous emission from one of the emissive states of the chiral enantiopure molecule will have an excess of either the right or the left CP light. Both emissions of CP light are recorded, and the difference of intensity is plotted in function of the wavelength, giving the CPL spectra. To quantify this difference, the luminescence dissymmetry factor is introduced and defined as in Equation (MP1) where and are the intensities of right and left circularly polarized light, the difference of intensity of RCP and LCP and the total intensity of emitted light.

(MP1)

As seen in this equation, if the value of the is of ±2 the emission will consist only of RCP (Right CP) or LCP (Left CP). Following this, if then must be equal to , resulting in an unpolarised emission. The luminescence dissymmetry factor can be rewritten using the rotatory strength normalised by, the dipole strength because of the dependence on the quantum yield (QY). In , , the magnitude of the electric transition quadrupole moment, is neglected as it is orders of magnitude smaller than the electric transition dipole moment (ED). is the magnitude the ED and the magnitude of the magnetic transition dipole moment (MD). Finally, represents the angle betweenand. The luminescence dissymmetry factor can now be expressed as in Equation (MP2).[6b]

(MP2)

(MP3)

It is worth mentioning that in the literature, Equation (MP2) is often seen with only the electric contribution in the denominator as for MD-forbidden / ED-allowed transitions, .[37] In this equation, the factor of 4 is arising from multiplicative factors in the expression of the intensities and.[38] This equation can be rewritten using the ratio, giving the Equation (MP3).[39]

**Figure MP1:** Energy level diagram for a Cr(III)N6 ion in octahedral symmetry. The two spin-flip emissions are shown in red on the right and the electronic configuration of the states is described on the left.



Taking into account these equations, to maximise. the magnitude of the two vectors should be similar, resulting in a ratio close to one and the vectors should be nearly collinear, causing to be close to one. As for MD-forbidden / ED-allowed transitions, one must investigate ED-forbidden / MD-allowed transitions to get in the range of . Laporte forbidden transitions as the f-f intrashell transitions (ΔL =0). Because of the interest towards cheaper and earth-abundant d-block metals, the focus will be laid on 3d cores. However, pure metal centered emissions from the 3d metal centers is less common than in 4f elements because of the vibration coupling and mixing of the orbitals of the ligands with the metal. Therefore, an electronic transition with an almost pure d-d character with a big enough energy gap between the levels to avoid back intersystem crossing (BISC). Closed shell d10 cores (Zn(II) and Cu(I)) are used but their dissymmetry factor remained small in the range from 10-2 to 10-4 as the emission arises from the ligand.[40] Open shell cores were therefore studied and measurements of Mn(II) in solid state[41] and Cr(III) were reported. To use such complexes, chiral resolution of the complex must be achieved which makes the inertness of the complex a new limiting factor . The field of reseach thus narrows down to Cr(III). With d3 configuration in a strong ligand field complex, the two Cr(2E → 4A2) and Cr(2T1 → 4A2) spin-flip transitions seems to be of interest. With the help of Figure MP1, one can see the electronic configuration of the excited states explaining the nature of the forbidden spin-flip transitions (ΔL = 0, ΔS ≠ 0). These two transitions therefore fulfil the conditions to maximise.

4. Chiroptical properiest of Cr(III) complexes

Rapidly after the ruby laser development by Maiman[13] ~~[20]~~, chiral Cr(III) complexes drew interest with their chiroptical properties in CD and CPL. Early examples in the late 1960s of tris-didentate chiral complexes such as (-)-[Cr(en)3]3+ (helical chirality) were separated and then measured (= -0.046 (14900 cm-1); Δεmax= -1.44 (21750 cm-1))[2a]. Notably Kaizaki *et al.* then studied many homoleptic and heteroleptic compounds with helical chirality such as (+)546-[Cr(pn)3]3+ (Δεmax= +0.34M−1cm−1 (20900 cm-1)) or (-)589-[Cr(ox)(bpy)(phen)]3+ (Δεmax= -1.76M−1cm−1 (20500 cm-1))[43]. Maybe because of the limitations of the instrument, such as the sensitivity or accessibility or because some complexes were not emissive, not a lot of CPL measurements are reported whereas CD spectrum were almost systematically recorded. It was only near the turn of the century that chirality arising from stereogenic center on the ligand itself was studied in CD and CPL on monometallic complexes by Tsubomura *et al.* using Λ-*fac*-[Cr(L-ala)3]3+ (= -0.021 (14185 cm-1))[27]. This complex displays values in the same range as observed for helical chirality. Contrariwise to enantiomers with helical chirality, separation of these is not compulsory for measuring their CD and CPL spectrum. Only recently a new type of chirality started to be exploited with Cr(III) cores in the field of CD and CPL. Although rigid tridentate ligands form achiral complexes, flexible 6-membered ring tridentate ligands were complexed to Cr(III) to be subsequently separated and studied in CD and CPL. Striking results in terms of came out of this new family of compounds overcoming as well the limiting factor of low QY in pioneer Cr(III) complexes such as [Cr(tpy)2]3+ (0.37%)[42]. The homoleptic complexes [Cr(ddpd)2]3+ and [Cr(dqp)2]3+ allowed to reach high QY in water of 11% and 5.2% respectively.[16]Using such complexes, high dissymmetry factor was observed. [Cr(dqp)2]3+ displayed a of 0.2 and 0.1 for the Cr(2E → 4A2)and Cr(2T1 → 4A2) transitions respectively[16a]. These values are the highest reported up to date for a Cr(III) complex and are comparable to lanthanide-based chiral complexes. The observed properties make the Cr(III) complexes potential sensitizers for CPL applications such as CPL lasers or CP-OLEDs. Cr(III) complexes for those at least a CD or a CPL spectra has been recorded are compiled in Table MP1.

**Table MP1:** Cr(III) complexes in octahedral geometry. Only separated complexes where either their CD or CPL or both spectra have been recorded.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex | CD: Δε (M−1 cm−1) | CPL | X-Ray structure | Ref. | |
| [Cr(CN)4(*d*-pn)] | +0.075 (22660 cm-1)  -0.384 (25540 cm-1)  +0.052 (32260 cm-1) | No | No | [25] | |
| [Cr(CN)4(*l*-pn)] | -0.081 (22620 cm-1)  +0.383 (25410 cm-1)  -0.059 (30170 cm-1) | No | No | [25] | |
| Λ-*cis*-(-)598-[Cr(CN)2(*d*-pn)2] | +0.484 (21810 cm-1)  -0.196 (24210 cm-1)  +0.040 (28410 cm-1) | No | Yes[44] | [25, 44-45] | |
| *cis*-(-)598-[Cr(CN)2(*l*-pn)2] | -0.557 (21880 cm-1)  +0.219 (24240 cm-1)  -0.059 (28330 cm-1) | No | No | [25] | |
| *cis*-(+)598-[Cr(CN)2(*d*-pn)(*l*-pn)] | +0.580 (23530 cm-1)  -0.045 (29590 cm-1) | No | No | [25] | |
| *cis*-(-)598-[Cr(CN)2(*d*-pn)(*l*-pn)] | -0.573 (23530 cm-1)  +0.050 (29590 cm-1) | No | No | [25] | |
| *cis*-(+)598-[Cr(CN)2(en)2] | +0.00065 (14510 cm-1)  -0.00072 (14750 cm-1)  +0.51 (23330 cm-1)  -0.036 (29850 cm-1) | No | No | [25, 46] | |
| (-)546-[Cr(en)3]  en = ethylenediamine | -0.016 (14950 cm-1)  +0.007 (15250 cm-1)  -0.007 (15550 cm-1)  -1.44 (21750 cm-1) [47] | -0.046 (14900 cm-1)[47] | Yes[48] | [47-48] | |
| (+)546-[Cr(en)3] | +0.0089 (15000 cm-1)  -0.0057 (15500 cm-1)  +0.0068 (15800 cm-1)  +1.49 (21900 cm-1)[43] | +0.028 (14880 cm-1)[2a] [a] | Yes[48] | [2a, 43, 48] | |
| (+)546-[Cr(phen)3]  phen = phenantroline | +0.0128 (13800 cm-1)  -0.0077 (14500 cm-1)  +2.48 (21900 cm-1) | No | Yes[49] | [43, 49] | |
| Δ-[Cr(bpy)3]  bpy = 2,2’-bipyridine | -1.2 (21739 cm-1)  -19.5 (28090 cm-1)  -21 (28818 cm-1)  -75 (31746 cm-1)  9.5 (34898 cm-1)  9 (35714 cm-1)  12 (37879 cm-1)[50] | No | Yes[51] | [50-51] | |
| Λ-[Cr(ox)3]  ox = oxalate | Yes | No | Yes[52] | [52-53] | |
| Λ-[Cr(mal)3]  Mal = malonate | Yes | No | No | [53] | |
| Λ-[Cr(thiox)3]  Thiox = dithioxalate | Yes | No | No | [53] | |
| [Cr(Oacac)3]  Oacac = 3-octylpentane-2,4-dionato | g= Δε/ε =  -0.04 (18868 cm-1)  +0.025 (15798 cm-1) [54]  −10 (11765 cm-1)  −50 (∼28570 cm-1) [36] | No | Yes[36] | [36, 54] | |
| [Cr(3-Buacac)3]  Buacac = 3-butylpentane-2,4-dionato | g= Δε/ε =  -0.05 (19048 cm-1)  0.032 (15798 cm-1) [55]  −40 (∼28570 cm-1) [36] | No | Yes[36] | [36, 55] | |
| [Cr(Pracac)3]  Pracac = 3-Propylpentane-2,4-dionato | g= Δε/ε =  −0.05 (19048 cm-1)  +0.032 (15798 cm-1) | No | No | | [56] |
| [Cr(Peacac)3]  Peacac = 3-Pentylpentane-2,4-dionato | g= Δε/ε =  −0.05 (19048 cm-1)  +0.032 (15798 cm-1) | No | No | | [56] |
| [Cr(en)3][Cr(ox)3] double salt | Yes | +0.008 (14131 cm-1 ) | Yes[57] | | [57-58] |
| [Cr(pn)3][Cr(ox)3] double salt  pn = propylendiamine | Yes | No | Yes | | [58] |
| (+)546-[Cr(pn)3] | +0.0022 (15100 cm-1)  -0.0005 (15600 cm-1)  +0.0011 (15900 cm-1)  +0.34 (20900 cm-1) | No | No | | [43] |
| (+)546-[Cr(ox)2(en)] | +0.0075 (14500 cm-1)  -0.00103 (14900 cm-1)  +0.00113 (15300 cm-1)  -0.05 (16800 cm-1)  +2.00 (19400 cm-1) | No | Yes[57] | | [43, 57] |
| (+)589-[Cr(ox)2(bpy)] | +0.0045 (13900 cm-1)  -0.0054 (14300 cm-1)  -0.0066 (14500 cm-1)  +0.0017 (14800 cm-1)  -0.12 (17000 cm-1)  +2.22 (19500 cm-1) | No | No | | [43] |
| (+)546-[Cr(ox)2(phen)] | +0.032 (13900 cm-1)  -0.0030 (14400 cm-1)  +0.027 (14700 cm-1)  -0.135 (16400 cm-1)  +2.46 (19000 cm-1) | No | No | | [43] |
| (+)546-[Cr(ox)(en)2] | +0.0129 (14700 cm-1)  -0.0064 (15200 cm-1)  +0.0114 (15500 cm-1)  +1.97 (20800 cm-1) | No | No | | [43] |
| (+)546-[Cr(ox)(bpy)2] | +0.0056 (13600 cm-1)  -0.0017 (14000 cm-1)  -0.0030 (14300 cm-1)  +0.0020 (14900 cm-1)  -0.06 (17800 cm-1)  +1.40 (20600 cm-1) | No | No | | [43] |
| (+)589-[Cr(ox)(phen)2] | +0.0046 (13800 cm-1)  -0.0062 (14800 cm-1)  -0.84 (18400 cm-1)  +1.50 (21200 cm-1) | No | No | | [43] |
| (-)589- [Cr(ox)(bpy)(phen)] | -0.0052 (13600 cm-1)  +0.0021 (14300 cm-1)  -1.76 (20500 cm-1) | No | No | | [43] |
| (-)589-[Cr(biguanide)3] | -0.008 (13100 cm-1)  +0.004 (14100 cm-1)  -2.78 (19200 cm-1)  +4.16 (21700 cm-1) | No | No | | [43] |
| (+)546-[Cr(acac)(en)2]  acac = acetylacetonate | +0.010 (13800 cm-1)  -0.0013 (14200 cm-1)  +0.077 (15200 cm-1)  +2.75 (21100 cm-1) | No | No | | [43] |
| (+)546-[Cr(acaCl)(en)2]  acaCl = 3-chloroacetylacetonato | +0.0078 (13700 cm-1)  -0.0032 (14200 cm-1)  +0.069 (15100 cm-1)  +2.62 (21100 cm-1) | No | No | | [43] |
| (+)546-[Cr(acaBr)(en)2]  acaBr = 3-bromoacetylacetonato | +0.0054 (13700 cm-1)  -0.0056 (14200 cm-1)  +0.048 (15200 cm-1)  +2.38 (21200 cm-1) | No | No | | [43] |
| (+)546-[Cr(acac)2(en)] | -0.0119 (12900 cm-1)  +0.056 (13900 cm-1)  -0.0224 (14400 cm-1)  -0.84 (17700 cm-1)  +4.00 (20100 cm-1) | No | No | | [43] |
| (+)546-[Cr(acac)(acaBr)(en)] | -0.0139 (12700 cm-1)  +0.0483 (13800 cm-1)  -0.0543 (14400 cm-1)  -0.84 (17700 cm-1)  +3.59 (20100 cm-1) | No | No | | [43] |
| (+)546-[Cr(acaBr)2(en)] | -0.88 (17300 cm-1)  +4.40 (20200 cm-1) | No | No | | [43] |
| (+)546-[Cr(acaCl)2(en)] | -0.0252 (12600 cm-1)  +0.0545 (13700 cm-1)  -0.0603 (14500 cm-1)  -0.86 (17700 cm-1)  +4.21 (20200 cm-1) | No | No | | [43] |
| Δ-(-)-[Cr(en)3]3+ doped in 2[Rh(en)3CI3]∙NaCl∙6H2O | Yes | -0.19 (14900 cm-1) | Yes | | [59] |
| (+)589-[Cr(gly)(en)2]  gly = glycine | +0.00777 (14810 cm-1)  -0.00158 (15150 cm-1)  +0.00604 (15580 cm-1)  +1.91 (21460 cm-1)  -0.16 (27550 cm-1)  +0.04 (30450 cm-1) | No | No | | [60] |
| (+)589-[Cr(L-ala)(en)2]  ala = alanine | +0.00664 (14770 cm-1)  -0.00125 (15280 cm-1)  +0.00270 (15570 cm-1)  +1.65 (21150 cm-1)  -0.12 (27700 cm-1)  +0.04 (30400 cm-1) | No | No | | [60] |
| (+)589-[Cr(phala)(en)2]  phala = phenylalanine | +0.00725 (14750 cm-1)  -0.00118 (15200 cm-1)  +0.00385 (15520 cm-1)  +1.70 (21100 cm-1)  -0.16 (27620 cm-1)  +0.03 (30530 cm-1) | No | No | | [60] |
| Λ-*fac*-[Cr(L-ala)3] | Yes | -0.021 (14185 cm-1)[b] | No | | [27] |
| [Cr(D-ala)3] | Yes | +0.024 (14185 cm-1)[b] | No | | [27] |
| (+)598-[Cr(*d*-pn)3]∙H2O | +1.805 (21230 cm-1)  -0.040 (24390 cm-1)  +0.095 (27400 cm-1)  +0.103 (29670 cm-1) | No | No | | [25] |
| (-)598-[Cr(*l*-pn)3]∙H2O | -1.792 (21230 cm-1)  +0.041 (24390 cm-1)  -0.098 (27250 cm-1)  -0.112 (29410 cm-1) | No | No | | [25] |
| Δ-(+)589-Cr[(-)(R,R)bdtp]3  bdtp = cyclic O,O’1(R), 2(R)-dimethyl-ethyene dithiophosphate | Yes | No | No | | [61] |
| (*M*,*M*)-[Cr(ddpd)2]  ddpd = (N,N’-dimethyl-N,N’-dipyridine-2-yl-pyridine-2,6-diamine) | Yes  Maximum at 300nm | -0.093 (12900 cm-1) | Yes | | [16b, 28] |
| (*P*,*P*)-(+)-[Cr(dqp)2]  dqp = (2,6-di(quinolin-8-yl)pyridine) | ∼90 (31447 cm-1)  ∼110 (24155 cm-1) | +0.2 (13351 cm-1)  -0.1 (13736 cm-1) | Yes | | [16a] |
| (*P*,*P*)-[Cr(dqpOMe)2]  dqpOMe = 4-methoxy-2,6-di(quinolin-8-yl)pyridine | ∼90 (∼30300 cm-1)  ∼100 (∼25000 cm-1) | +0.18 (13228 cm-1)  -0.08 (13831 cm-1) | Yes | | [29] |
| (*P*,*P*)-[Cr(dqpBr)2]  dqpBr = 4-bromo-2,6-di(quinolin-8-yl)pyridine | ∼90 (∼30300 cm-1)  ∼100 (∼24400 cm-1) | +0.19 (13316 cm-1)  -0.07 (13870 cm-1) | Yes | | [29] |
| (*P*,*P*)-[Cr(dqpC≡CH)2]  dqpC≡CH = 4-Alkyne-2,6-di(quinolin-8-yl)pyridine | ∼110 (∼30300 cm-1)  ∼100 (∼24400 cm-1) | +0.17 (13280 cm-1)  -0.06 (13850 cm-1) | Yes | | [29] |
| Λ-(-)598-*trans-*(O5O6)-[Cr(eda3p)]  eda3p = ethylenediamine-N-acetato-N,N’,N’-tri-3-propionate | +0.09 (16580 cm-1)  -0.64 (18760 cm-1)  -0.14 (21050 cm-1)  +0.07 (23530 cm-1)  +0.23 (26670 cm-1) | No | No | | [62] |
| Λ-(-)598-*trans-*(O5)-[Cr(eddda)]  Eddda = Ethylenediamine-N,N’-diacetato-N,N’-dipropionate | +0.0352 (14250 cm-1)  -0.0092 (14870 cm-1)  +0.0780 (15260 cm-1)  +0.207 (16530 cm-1)  -0.765 (18620 cm-1)  -0.19 (20330 cm-1)  -0.05 (22170 cm-1)  -0.075 (24100 cm-1)  +0.23 (26530 cm-1) | No | No | | [63] |
| Λ-(+)598-*trans-*(O5)-[Cr(S,S-edds)]  S,S-edds = (S,S)-2,2’-(ethylenediimino) disuccinate | +0.0348 (14210 cm-1)  -0.0024 (14380 cm-1)  +0.0036 (14530 cm-1)  -0.0120 (14870 cm-1)  +0.0690 (15440 cm-1)  +0.409 (17540 cm-1)  -0.396 (19330 cm-1)  +0.453 (21830 cm-1)  +0.33 (23330 cm-1)  +0.386 (27030 cm-1) | No | No | | [63] |
| Λ-(+)598-[Cr(S,S-ptnta)]  S,S-ptnta = (2S,4S)-2,4-pentanediamine tetraacetate | -0.0038 (13920 cm-1)  +0.0055 (14350 cm-1)  +0.0058 (14460cm-1)  -0.0017 (14620 cm-1)  +0.0014 (14620 cm-1)  -0.0021 (15000 cm-1)  +0.0260 (15310 cm-1)  +0.2 (18000 cm-1)  +0.442 (19670 cm-1)  -0.064 (21670 cm-1)  +0.435 (24000 cm-1)  +0.27 (25250 cm-1)  -0.024 (29660 cm-1) | No | No | | [63a] |
| (-)589-[Cr2(OH)2(bpy)2(phen)2] | -0.0766 (13700 cm-1)  -0.0920 (14100 cm-1)  +0.0083 (15500 cm-1)  -6.82 (18700 cm-1) | No | No | | [43] |
| [Cr2(l-tart2H)(bpy)2]  l-tart= L-tartrate | Yes | No | No | | [64] |
| [Cr2(l-tart2H)(phen)2] | Yes | No | Yes | | [64-65] |
| [Cr2(OH)2(L-ala)4] | Yes | Yes[b] | No | | [60] |
| *M*-(+)589-[Cr(L)3]3+  L = | -22 (31750 cm-1)  +48 (29070 cm-1)  +1.8 (21500 cm-1) | No | No | | [33] |
| *(M*,*M*)-(-)589-[LnCr(L)3]6+ Ln = Eu, Gd, Tb | -74 (29410 cm-1) | +0.01 (13423 cm-1)  +0.07 (16234 cm-1)  (identical for all Ln) | Yes for Eu | | [33] |
| (Λ)- and (Δ)-[(acac)2Cr(ox)Ln(HBpz3)2]  Ln= Yb, Dy, Sm, Ho, Er  HBpz3- = hydrotris(pyrazol-1-yl)borato | Yes | No | Yes for Yb, Sm, Ho and Er | | [66] |

[a] Measurement done in a solid at -78°C, [b] Measurement done at 77K

Conclusions and perspectives

Since the beginning of modern coordination chemistry and photophysics, Cr(III) complexes have played an essential role in the development of these two correlated branches. This is mainly due to their kinetic inertness against ligand substitution and their light emission arising from the metal centered Cr(2E) and Cr(2T1) states.

The field of CPL is mainly dominated by chiral organic chromophores and chiral metal complexes based on 4d, 5d and 4f elements. Recent results have demonstrated that chiral Cr(III) complexes have also a great potential, because chromium is a earth-abundant metal and because the electronic nature of the radiative Cr(2T1) and Cr(2E) transitions fit the conditions to enhance the dissymmetric factor *g*lum. Up to now, the record value reported for a chiral Cr(III) of *g*lum is only about 0.2 which indicates that there is still a huge gap to reach the maximized values of ±2. This promising result together with the few literature reports on chiral Cr(III) complexes indicate that efforts should be made on the preparation of these chiral complexes. It is worth mentioning that computational calculations are as well fairly underexplored. Insights on computational theory are fundamentally important and should facilitate the rational design of chiral Cr(III) complexes. As shown in Table MP1, all the examples concerning chiral Cr(III) complexes reported so far are restricted to discrete mononuclear complexes. It would be of interest to study how chiral Cr(III) complexes behave in supramolecular structures or more sophisticated assemblies where additional sources of chirality can be present. Moreover, the kinetic inertness of Cr(III) complexes should allow the manipulation for their insertion in complex matrices or platforms like polymers where other phenomenon like exciton-coupling or long-range chirality can enhance the chiroptical properties.

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