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

Author(s), Maxime Poncet,[a] Amina Benchohra,\*[a]Juan-Ramón Jiménez\*[a],[b] 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: [Amina.Benchohra@unige.ch](mailto:Amina.Benchohra@unige.ch); [Claude.Piguet@unige.ch](mailto: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 chemistry due to their potential applications in emerging fields such as spintronics and photonics. Beyond the largely exploited p-block, 4d/5d-block and f-block chiral entities, chiral 3d-block Cr(III) complexes have recently attracted interest because of its abundancy in the earth crust, its kinetic inertness and its promising metal-centered Cr(2E) and Cr(2T1) phosphorescence. The associated spin-flip transitions could provide large dissymmetric factor (*g*lum) and high luminescence quantum yields (**) when six-membered strong-field chelate rings are coordinated to chiral six-coordinate Cr(III). 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 for witch their chiroptical have been investigated. The promising electronic properties of these complexes together with their low cost make these underexplored systems appealing candidates for CPL applications.

1. Introduction

Circularly Polarized Luminescence (CPL), which is the emission of polarized light with a certain degree of handedness from a chiral luminophore upon non-polarized light excitation, has attracted the attention of chemists and physicists since 1948 when Samoilov observed this phenomenon in a crystal of sodium uranyl acetate.[1] Later, Oosterhof and Emeis reported the first CPL measurements recorded in solution for a trans-β-hydrindanone chromophore and for the coordination complex [Cr(en)3]3+, where en stands for ethylenediamine.[2] Currently, the research devoted to CPL is boosted by the need for chiroptical features in a wide range of applications which spans from technological (security inks, CP-OLED)[3] to biological applications (molecular probes, bioimaging, chiral recognition)[4].

Major activity in the field of CPL has been focused on the development of chiral chromophores such as organic dyes,[5] 4d and 5d metal complexes,[5a, 5b] lanthanides-based complexes[6] and more sophisticated supramolecular/macromolecular architectures.[7] The latter approach seems to emerge as a novel strategy for enhancing *g*lum in organic systems[8] because efficient CPL emitters require large dissymmetry factors (*g*lum) and high quantum yields (*φ*).[5c] The first parameter is related to the degree of “enantiorichness” of the circularly polarized 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 (Equation 1 with or ). The second parameter, i.e. the quantum yield *φ*, states that the ratio of emitted over absorbed photons should be also maximized. As it is regularly reminded, 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 quantum yields arising from intense Metal-to-Ligand Charge Transfer or Ligand-to-metal Charge transfer and π\* → π transitions, which can compensate somehow their low *g*lum. In addition, their considerable kinetic inertness makes those systems still attractive candidates for applications.

In this context, the maximization of *g*lum in a chiral molecule requires the operation of electrically forbidden and magnetically allowed electronic transitions (Equation 2), a situation encountered for intrashell f-f and d-d transitions in the free ions.[9] Transposed to molecular systems, the success of these predictions can be mainly assessed in lanthanide-containing complexes where the crystal-field effects are minimized with the establishment of the current record value of *g*lum = +1.38 at 595 nm for Cs[Eu[(+)-(hfbc)4] (hfbc = (+)-3-heptafluorobutylyryl-camphorato) in solution at room temperature.[10] However, the high cost for the extraction and purification or rare earth together with their intrinsic kinetic lability are not negligible shortcomings for potential applications. Currently, the research of photoactive molecules based on earth-abundant metals (basically first-row 3d-block metals) is an emerging area because they represent a realistic alternative to precious metals (Ru, Ir, Pt or Au) and to 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 limitation.[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 indeed among the most investigated coordination complexes in photophysics. Because of their kinetic inertness (large crystal field stabilization energy for the d3 electronic configuration)[14] and their sharp NIR electric-dipole (Laporte) and spin forbidden Cr(2E→4A2) and Cr(2T1→4A2) emissions when embedded into strong ligand field environments,[13-14,15] these metal complexes open new avenues for the development of CPL emitters based on cheap metals.[16]

This mini-review reports on the chiral Cr(III) complexes, for which the chiroptical properties have been recorded and discussed.

2. Chirality in Cr(III) complexes

General chirality definition relates to the geometric property of an object of not being superimposable with 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 domain 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) complexes noticeably demonstrate it, with chirality 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 while tuning ligand denticities, flexibilities, symmetries as well as coordination modes. A general description of these points is outlined below for seelcted Cr(III) compounds containing: (i) achiral planar ligands, (ii) stereogenic ligands and (iii) achiral flexible ligands inducing chirality upon complexation. 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 in [CrA6] leads to the highest accessible symmetry *O*h, which is achiral. The successive replacements of A with different B ligands exclusively lead to the formation of achiral compounds with reduced-symmetry. Each heteroleptic complex [CrA4B2] and [CrA3B3] has two geometrical isomers, cisoid (*cis*) and transoid (*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 ligands (A, B and C) about the metal center in [CrA*x*B*y*C6-*x*-*y*] that enables the emergence of chirality of central kind. However, examples of this type are very 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 (Figure 1a). Bis and tris-(chelate) complexes display a helicity (Δ or Λ) associated with the trigonal twist of the ligands. The highest chiral symmetry *D*3 is attained with homoleptic tris-chelate [Cr(A∩A)3] complexes, where A∩A is a symmetrical didentate chelating ligand such as the archetypal bipyridine, phenantroline or oxalate. The number of geometrical isomers increases when using unsymmetrical ligands A∩A’ as illustrated for the chiral [Cr(A∩A’)3] complex, which can exist as a *C*3-symmetrical *fac*-isomer or a *C*1-symmetrical *mer*-isomer (Figure 1a top). Further complications arise for heteroleptic tris-chelate complexes where [Cr(A∩A)2(B∩B)] indeed corresponds to a single chiral isomer (Figure 1a bottom), but [Cr(A∩A’)2(B∩B)] provides three different chiral isomers. Naturally, related analyses hold for the bis-chelate complexes [M(A∩A)2B2], which can exist as a chiral *cis*-[M(A∩A)2B2] isomer with *C*2-symmetry or as an alternative achiral *trans*-[M(A∩A)2B2] isomer with *D2h*  symmetry (Figure 1a bottom).



Figure 1. Schematic representation of selected homoleptic and heteroleptic six-coordinate Cr(III) complexes with a) didentate and b) tridentate chelate ligands.

Tridendate ligands (η3). Contrary to didentate ligands, tridendate planar ligands provide fewer opportunities to achieve chiral complexes (Figure 1b). For instance, the famous homoleptic bis(terpyridine) chromium(III) [Cr(tpy)2]3+ complex adopts the achiral *D*2d-symmetrical [Cr(*mer*-A∩A’∩A)2] arrangement[23] and the exceptionally luminescent [Cr(tpe)]3+ complex (tpe is the tripodal ligand 1,1,1-tris(pyrid-2-yl)ethane) belongs to the S6-symmetrical point group ([Cr(*fac*-A3)2] in Figure 1b top).[24] The situation does not significantly change for the heteroleptic *C*2v-symmetrical [Cr(*mer*-A∩A’∩A)(*mer*-B∩B’∩B)] and *C*3v-symmetrical [M(*fac*-A3)(*fac*-B3)] analogues (Figure 1b bottom). Chirality indeed emerges when unsymmetrical planar ligands are wrapped around the metal ion leading, for instance, to chiral *C*2-symmetrical [Cr(*mer*-A∩A’∩A’’)2] and [Cr(*fac*-A2A’)2] complexes (Figure 1b top). To the best of our knowledge no example of the latter two chiral complexes have been reported with Cr(III). Finally, non-planar multidendate ligands can enable complexes gaining dissymmetry, as discussed in section 2.3.

2.2. Chirality brought by chiral ligands

To circumvent non-chiral symmetries, the standard strategy consists 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(*R/S*-pn)(CN)4] compounds,[25] derived from the *C*2*v*-symmetrical achiral [Cr(A∩A)B4] building block. The central chirality of organic compounds was also combined with the complexes helical chirality (section 2.1 above) resulting in pairs of diastereomers, often with the added benefit of diastereoselective self-sorting and the use of conventional chromatography techniques for separation purpose. 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, surprisingly, the obtained crystallized compound display the opposite helical chirality Δ-(-)-[Cr(+)-(S)(S)-Mebdtp]. Diastereoisomeric crystallization was also early exploited withb the connection of amino-acids to 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 which are rigidified upon complexation. Non-planar ligands can thus undergo a conformational twist upon complexation which removes symmetry axes of the second kind (Figure 2). This deviation from planarity within individual ring gives rise to inert δ/λ ligand conformations. A striking example of this is given by the di(tridentate) ddpd ligand (= *N*,*N*’-dimethyl-*N*,*N*’-dipyridine-2-yl-pyridine-2,6-diamine)[28] in [Cr(ddpd)2]3+ and dqp ligand (= 2,6-di(quinolin-8-yl)pyridine)[16a] in [Cr(dqp)2]3+ complexes, in which the chiral helical structures result from the ligand twist upon complexation. 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, for [Cr(ddpd)2]3+ and [Cr(dqp)2]3+, only the pairs of enantiomers *PP*/*MM* could be observed in solution and in the solid state whereas the more constrained meso *PM* isomers are lacking.[29]. Concerning didentate chelates, and despite ethylenediamine (en) being 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 suggested that the pair of diasteroemers Λ-[Cr(δ-en)3]n+ and Δ-[Cr(λ-en)3]n+ is favored in the crystalline state.[30]

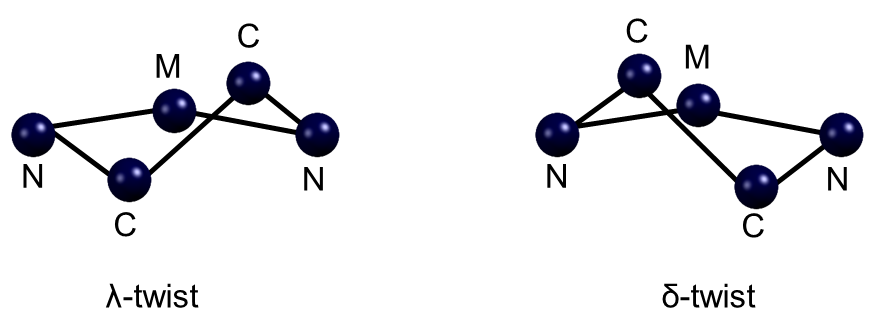


Figure 2. Chiral conformational twists of a five-membered flexible chelate ligand bound to a metal M.

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

Among the different chiroptical properties, circular dichroism (CD), which refers to the asymmetric absorption of circularly polarized light by optically active molecules, is one of the most used technique to empirically assign the chiral structure of small molecules or of secondary structures in proteins. The CD spectra are recorded as the difference in absorption of one circularly polarized light compared to the other, given as Δ*ε*, as a function of the incident wavelength. When the value of Δ*ε* goes from negative to positive, the effect is called positive Cotton Effect after its discoverer[31] and vice-versa for the opposite. CD is temperature, solvent and concentration dependent and must be handled with care when comparing results.[32] Furthermore, if the two recorded spectra are mirror images, it does not necessarily mean that each sample is enantiopure, but only that the ‘chiral content’ is identical and opposite in each mixture. Therefore, prior to CD measurements, a pertinent and quantitative chiral resolution is required if pure enantiomers are the target of the study. As enantiomers have the same physico-chemical properties in a standard achiral medium, such separation the racemate mixtures 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 light source, in a CPL measurement, the sample is irradiated with non-polarized light in an energy domain where the photons are absorbed by the sample. Spontaneous emission from one of the emissive states of the chiral enantiopure molecule will have an excess of either the right or the left circularly polarized light. Both emissions are recorded, and the difference of intensity is plotted in function of the wavelength, giving the CPL spectrum. To quantify this difference, the luminescence dissymmetry factor is introduced and defined in Equation (1) where and are the intensities of right and left circularly polarized emitted light, the difference in intensity and the total intensity of emitted light.

(1)

When = ±2, the emission will consist only of RCP (Right Circularly Polarized) or LCP (Left Circularly Polarized) emitted light. Accordingly, corresponds to = and unpolarised light emission. The luminescence dissymmetry factor can be rewritten using the rotatory strength normalised by the dipole strength (Equation 2 left). Both parameters can be related to the well-known electric and magnetic transition dipole moments together with the angle ** between them (Equation 2 centre).[6b] [37]

(2)

This equation can be rewritten for highlighting the ratio (Equation 2 right). Consequently, *g*lum reaches a maximum when (i) *r* =1 () and (ii) the vectors are collinear ( = 1).[38],[38]

In most cases, the intense emission bands correspond to ED-allowed transitions with and *g*lum is (desperately) weak as often found for organic chromophores. A cure requires ED-forbidden/MD-allowed transitions in order to get in the same range as . The Laporte forbidden f-f intrashell transitions (Δ*L* =0) fit these criteria and are therefore valuable candidates for producing high dissymmetry factors. Because of the interest of using cheaper and earth-abundant d-block metals, the focus will be laid on 3d cores. However, pure metal-centered emissions along the 3d-block series is less common than in 4f elements because of vibrational coupling and mixing of the orbitals of the ligands with those of the metal. Therefore, an electronic transition with an almost pure d-d character with a large enough energy gap is rare along the first transition series.



**Figure 2:** Energy level diagram for a [Cr(III)N]6 ion in octahedral symmetry. The two spin-flip emissions are shown in red on the right and the electronic configuration of the states is highlighted on the left.

Closed shell d10 cores (Zn(II) and Cu(I)) have been extensively used, but their dissymmetry factor remained small (10-2 ≤ *g*lum ≤ 10-4) as the emission involves ligand-centered levels.[39] Open shell cores were therefore studied and CPL activity could be measured for d-d transitions in Mn(II) [40] and in Cr(III).[40] However, chiral resolution of the complex is often required, which makes the inertness of the complex a new limiting factor and the field narrows down to Cr(III) in strong ligand field complexes. Thanks to its d3 electronic configuration, pseudo-octahedral [CrL6] chromophores display two magnetically-allowed but electric-dipole forbidden Cr(2E → 4A2) and Cr(2T1 → 4A2) spin-flip transitions (Δ*L* = 0, Δ*S* ≠ 0) which fulfil the conditions to maximise (Figure 2).

4. Chiroptical properties of Cr(III) complexes

Early examples of tris-didentate chiral complexes, such as (-)-[Cr(en)3]3+ (helical chirality, section 2.3) were separated in the late 1960s and then characterized for their chirooptical properties (= -0.046 (14900 cm-1); Δ*ε*max= -1.44 (21750 cm-1)).[2a] Kaizaki *et al.* then studied many homoleptic and heteroleptic compounds with helical chirality such as (+)546-[Cr(pn)3]3+ (Δ*ε*max= +0.34M−1cm−1 (20900 cm-1), ) or (-)589-[Cr(ox)(bpy)(phen)]3+ (Δ*ε*max= -1.76M−1cm−1 (20500 cm-1)).[41] Maybe because of (i) a limited access to adapted instrumentation and (ii) some complexes were not emissive, only few CPL measurements have been reported whereas CD spectrum were systematically recorded (Table 1). It was only near the turn of the last century that chirality arising from stereogenic centers located on the ligand itself (see section 2.2) was studied by CD and CPL spectroscopy for monometallic chromium complexes in Λ-*fac*-[Cr(L-ala)3]3+ (= -0.021 (14185 cm-1))[42]. This complex displays dissymmetry factors in the same range as those observed for helical chirality. Contrariwise to enantiomers induced by helical chirality, chirality brought by chiral ligands does not require separation for measuring their CD and CPL spectrum. Recently, chirality arising from chelate rings conformation (see section 2.3) started to be systematically exploited with Cr(III) cores in the field of CD and CPL. Although rigid and planar tridentate 5-membered ring chelates form only achiral complexes, tridentate 6-membered ring chelates adopt helical conformation upon complexation to Cr(III) to give [Cr(ddpd)2]3+ and [Cr(dqp)2]3+.[16] Subsequent separation on chiral phases provided pure *PP* and *MM* enantiomers, for which large dissymmetry factor could be obtained with a record of of 0.2 and 0.1 for the Cr(2E → 4A2)and Cr(2T1 → 4A2) transitions in [Cr(dqp)2]3+.[16a]. These values are the highest reported to date for a Cr(III) complex and are comparable to those reported for lanthanide-based chiral complexes. The observed properties make these Cr(III) complexes potential sensitizers for CPL applications such as CPL lasers or CP-OLEDs. Chiral Cr(III) complexes for which a CD and/or a CPL spectra has been recorded are compiled in Table 1.

**Table 1** CD or CPL characteristics reported for chiral six-coordinate pseudo-octahedral Cr(III) complexes

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Entry | Complex | Chirality[a] | CD: Δ*ε* (M−1 cm−1) | CPL: *g*lum | X-ray structure | Ref. |
| 1 | [Cr(CN)4(*d*-pn)]  pn = 1,2-propylendiamine | 2.2 | +0.075 (22660 cm-1)  -0.384 (25540 cm-1)  +0.052 (32260 cm-1) | No | No | [25] |
| 2 | [Cr(CN)4(*l*-pn)]  pn = 1,2-propylendiamine | 2.2 | -0.081 (22620 cm-1)  +0.383 (25410 cm-1)  -0.059 (30170 cm-1) | No | No | [25] |
| 3 | Λ-*cis*-(-)598-[Cr(CN)2(*d*-pn)2]  pn = 1,2-propylendiamine | 2.2 | +0.484 (21810 cm-1)  -0.196 (24210 cm-1)  +0.040 (28410 cm-1) | No | Yes[43] | [25, 43-44] |
| 4 | *cis*-(-)598-[Cr(CN)2(*l*-pn)2]  pn = 1,2-propylendiamine | 2.2 | -0.557 (21880 cm-1)  +0.219 (24240 cm-1)  -0.059 (28330 cm-1) | No | No | [25] |
| 5 | *cis*-(+)598-[Cr(CN)2(*d*-pn)(*l*-pn)]  pn = 1,2-propylendiamine | 2.2 | +0.580 (23530 cm-1)  -0.045 (29590 cm-1) | No | No | [25] |
| 6 | *cis*-(-)598-[Cr(CN)2(*d*-pn)(*l*-pn)]  pn = 1,2-propylendiamine | 2.2 | -0.573 (23530 cm-1)  +0.050 (29590 cm-1) | No | No | [25] |
| 7 | *cis*-(+)598-[Cr(CN)2(en)2] | 2.1, 2.3 | +0.00065 (14510 cm-1)  -0.00072 (14750 cm-1)  +0.51 (23330 cm-1)  -0.036 (29850 cm-1) | No | No | [25, 45] |
| 8 | (-)546-[Cr(en)3]  en = ethylenediamine | 2.1, 2.3 | -0.016 (14950 cm-1)  +0.007 (15250 cm-1)  -0.007 (15550 cm-1)  -1.44 (21750 cm-1) [46] | -0.046 (14900 cm-1)[46] | Yes[47] | [46-47] |
| 9 | (+)546-[Cr(en)3] | 2.1, 2.3 | +0.0089 (15000 cm-1)  -0.0057 (15500 cm-1)  +0.0068 (15800 cm-1)  +1.49 (21900 cm-1)[41] | +0.028 (14880 cm-1)[2a] [b] | Yes[47] | [2a, 41, 47] |
| 10 | (+)546-[Cr(phen)3]  phen = phenantroline | 2.1 | +0.0128 (13800 cm-1)  -0.0077 (14500 cm-1)  +2.48 (21900 cm-1) | No | Yes[48] | [41, 48] |
| 11 | Δ-[Cr(bpy)3]  bpy = 2,2’-bipyridine | 2.1 | -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)[49] | No | Yes[50] | [49-50] |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 12 | Λ-[Cr(ox)3]  ox = oxalate | 2.1 | Yes | No | Yes[51] | [51-52] |
| 13 | Λ-[Cr(mal)3]  Mal = malonate | 2.1 | Yes | No | No | [52] |
| 14 | Λ-[Cr(thiox)3]  Thiox = dithioxalate | 2.1 | Yes | No | No | [52] |
| 15 | [Cr(Oacac)3]  Oacac = 3-octylpentane-2,4-dionato | 2.1 | *g* = Δ*ε*/*ε* =  -0.04 (18868 cm-1)  +0.025 (15798 cm-1) [53]  −10 (11765 cm-1)  −50 (∼28570 cm-1) [36] | No | Yes[36] | [36, 53] |
| 16 | [Cr(3-Buacac)3]  Buacac = 3-butylpentane-2,4-dionato | 2.1 | *g* = Δ*ε*/*ε* =  -0.05 (19048 cm-1)  0.032 (15798 cm-1) [54]  −40 (∼28570 cm-1) [36] | No | Yes[36] | [36, 54] |
| 17 | [Cr(Pracac)3]  Pracac = 3-Propylpentane-2,4-dionato | 2.1 | *g*= Δ*ε*/*ε* =  −0.05 (19048 cm-1)  +0.032 (15798 cm-1) | No | No | [55] |
| 18 | [Cr(Peacac)3]  Peacac = 3-Pentylpentane-2,4-dionato | 2.1 | *g* = Δ*ε*/*ε* =  −0.05 (19048 cm-1)  +0.032 (15798 cm-1) | No | No | [55] |
| 19 | [Cr(en)3][Cr(ox)3] double salt | 2.1, 2.3 | Yes | +0.008 (14131 cm-1 ) | Yes[56] | [56-57] |
| 20 | [Cr(pn)3][Cr(ox)3] double salt  pn = 1,3 propylendiamine | 2.1, 2.3 | Yes | No | Yes | [57] |
| 21 | (+)546-[Cr(pn)3]  pn = 1,3 propylendiamine | 2.1, 2.3 | +0.0022 (15100 cm-1)  -0.0005 (15600 cm-1)  +0.0011 (15900 cm-1)  +0.34 (20900 cm-1) | No | No | [41] |
| 22 | (+)546-[Cr(ox)2(en)] | 2.1, 2.3 | +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[56] | [41, 56] |
| 23 | (+)589-[Cr(ox)2(bpy)] | 2.1 | +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 | [41] |
| 24 | (+)546-[Cr(ox)2(phen)] | 2.1 | +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 | [41] |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 25 | (+)546-[Cr(ox)(en)2] | 2.1, 2.3 | +0.0129 (14700 cm-1)  -0.0064 (15200 cm-1)  +0.0114 (15500 cm-1)  +1.97 (20800 cm-1) | No | No | [41] |
| 26 | (+)546-[Cr(ox)(bpy)2] | 2.1 | +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 | [41] |
| 27 | (+)589-[Cr(ox)(phen)2] | 2.1 | +0.0046 (13800 cm-1)  -0.0062 (14800 cm-1)  -0.84 (18400 cm-1)  +1.50 (21200 cm-1) | No | No | [41] |
| 28 | (-)589- [Cr(ox)(bpy)(phen)] | 2.1 | -0.0052 (13600 cm-1)  +0.0021 (14300 cm-1)  -1.76 (20500 cm-1) | No | No | [41] |
| 29 | (-)589-[Cr(biguanide)3] | 2.1 | -0.008 (13100 cm-1)  +0.004 (14100 cm-1)  -2.78 (19200 cm-1)  +4.16 (21700 cm-1) | No | No | [41] |
| 30 | (+)546-[Cr(acac)(en)2]  acac = acetylacetonate | 2.1, 2.3 | +0.010 (13800 cm-1)  -0.0013 (14200 cm-1)  +0.077 (15200 cm-1)  +2.75 (21100 cm-1) | No | No | [41] |
| 31 | (+)546-[Cr(acaCl)(en)2]  acaCl = 3-chloroacetylacetonato | 2.1, 2.3 | +0.0078 (13700 cm-1)  -0.0032 (14200 cm-1)  +0.069 (15100 cm-1)  +2.62 (21100 cm-1) | No | No | [41] |
| 32 | (+)546-[Cr(acaBr)(en)2  acaBr = 3-bromoacetylacetonato | 2.1, 2.3 | +0.0054 (13700 cm-1)  -0.0056 (14200 cm-1)  +0.048 (15200 cm-1)  +2.38 (21200 cm-1) | No | No | [41] |
| 33 | (+)546-[Cr(acac)2(en)] | 2.1, 2.3 | -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 | [41] |
| 34 | (+)546-[Cr(acac)(acaBr)(en)] | 2.1, 2.3 | -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 | [41] |
| 35 | (+)546-[Cr(acaBr)2(en)] | 2.1, 2.3 | -0.88 (17300 cm-1)  +4.40 (20200 cm-1) | No | No | [41] |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 36 | (+)546-[Cr(acaCl)2(en)] | 2.1, 2.3 | -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 | [41] |
| 37 | Δ-(-)-[Cr(en)3]3+ doped in 2[Rh(en)3CI3]∙NaCl∙6H2O | 2.1, 2.3 | Yes | -0.19 (14900 cm-1) | Yes | [58] |
| 38 | (+)589-[Cr(gly)(en)2]  gly = glycine | 2.1, 2.3 | +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 | [59] |
| 39 | (+)589-[Cr(L-ala)(en)2]  ala = alanine | 2.1, 2.2, 2.3 | +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 | [59] |
| 40 | (+)589-[Cr(phala)(en)2]  phala = phenylalanine | 2.1, 2.2, 2.3 | +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 | [59] |
| 41 | Λ-*fac*-[Cr(L-ala)3] | 2.1, 2.2 | Yes | -0.021 (14185 cm-1)[c] | No | [42] |
| 42 | [Cr(D-ala)3] | 2.1, 2.2 | Yes | +0.024 (14185 cm-1)[c] | No | [42] |
| 43 | (+)598-[Cr(*d*-pn)3]  pn = 1,2-propylendiamine | 2.1, 2.2 | +1.805 (21230 cm-1)  -0.040 (24390 cm-1)  +0.095 (27400 cm-1)  +0.103 (29670 cm-1) | No | No | [25] |
| 44 | (-)598-[Cr(*l*-pn)3]  pn = 1,2-propylendiamine | 2.1, 2.2 | -1.792 (21230 cm-1)  +0.041 (24390 cm-1)  -0.098 (27250 cm-1)  -0.112 (29410 cm-1) | No | No | [25] |
| 45 | Δ-(+)589-Cr[(-)(R,R)bdtp]3  bdtp = cyclic O,O’1(R), 2(R)-dimethyl-ethylene dithiophosphate | 2.1, 2.2 | Yes | No | No | [60] |
| 46 | (*M*,*M*)-[Cr(ddpd)2]  ddpd = (N,N’-dimethyl-N,N’-dipyridine-2-yl-pyridine-2,6-diamine) | 2.3 | Yes  Maximum at 300nm | -0.093 (12900 cm-1) | Yes | [16b, 28] |
| 47 | (*P*,*P*)-(+)-[Cr(dqp)2]  dqp = (2,6-di(quinolin-8-yl)pyridine) | 2.3 | ∼90 (31447 cm-1)  ∼110 (24155 cm-1) | +0.2 (13351 cm-1)  -0.1 (13736 cm-1) | Yes | [16a] |
| 48 | (*P*,*P*)-[Cr(dqpOMe)2]  dqpOMe = 4-methoxy-2,6-di(quinolin-8-yl)pyridine | 2.3 | ∼90 (∼30300 cm-1)  ∼100 (∼25000 cm-1) | +0.18 (13228 cm-1)  -0.08 (13831 cm-1) | Yes | [29] |
| 49 | (*P*,*P*)-[Cr(dqpBr)2]  dqpBr = 4-bromo-2,6-di(quinolin-8-yl)pyridine | 2.3 | ∼90 (∼30300 cm-1)  ∼100 (∼24400 cm-1) | +0.19 (13316 cm-1)  -0.07 (13870 cm-1) | Yes | [29] |
| 50 | (*P*,*P*)-[Cr(dqpC≡CH)2]  dqpC≡CH = 4-Alkyne-2,6-di(quinolin-8-yl)pyridine | 2.3 | ∼110 (∼30300 cm-1)  ∼100 (∼24400 cm-1) | +0.17 (13280 cm-1)  -0.06 (13850 cm-1) | Yes | [29] |
| 51 | Λ-(-)598-*trans-*(O5O6)-[Cr(eda3p)]  eda3p = ethylenediamine-N-acetato-N,N’,N’-tri-3-propionate | 2.3 | +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 | [61] |
| 52 | Λ-(-)598-*trans-*(O5)-[Cr(eddda)]  Eddda = Ethylenediamine-N,N’-diacetato-N,N’-dipropionate | 2.3 | +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 | [62] |
| 53 | Λ-(+)598-*trans-*(O5)-[Cr(S,S-edds)]  S,S-edds = (S,S)-2,2’-(ethylenediimino) disuccinate | 2.2, 2.3 | +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 | [62] |
| 54 | Λ-(+)598-[Cr(S,S-ptnta)]  S,S-ptnta = (2S,4S)-2,4-pentanediamine tetraacetate | 2.2, 2.3 | -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 | [62a] |
| 55 | (-)589-[Cr2(OH)2(bpy)2(phen)2] | 2.1 | -0.0766 (13700 cm-1)  -0.0920 (14100 cm-1)  +0.0083 (15500 cm-1)  -6.82 (18700 cm-1) | No | No | [41] |
| 56 | [Cr2(l-tart2H)(bpy)2]  l-tart= L-tartrate | 2.1, 2.2 | Yes | No | No | [63] |
| 57 | [Cr2(l-tart2H)(phen)2] | 2.1, 2.2 | Yes | No | Yes | [63-64] |
| 58 | [Cr2(OH)2(L-ala)4] | 2.1, 2.2 | Yes | Yes[c] | No | [59] |
| 59 | *M*-(+)589-[Cr(L)3]3+  L = | 2.1 | -22 (31750 cm-1)  +48 (29070 cm-1)  +1.8 (21500 cm-1) | No | No | [33] |
| 60 | *(M*,*M*)-(-)589-[LnCr(L)3]6+ Ln = Eu, Gd, Tb | 2.1 | -74 (29410 cm-1) | +0.01 (13423 cm-1)  +0.07 (16234 cm-1)  (identical for all Ln) | Yes for Eu | [33] |
| 61 | (Λ)- and (Δ)-[(acac)2Cr(ox)Ln(HBpz3)2]  Ln= Yb, Dy, Sm, Ho, Er  HBpz3- = hydrotris(pyrazol-1-yl)borato | 2.1 | Yes | No | Yes for Yb, Sm, Ho and Er | [65] |

[a] Type of chirality defined in sections 2.1, 2.2 and 2.3. [b] Measurement done in a solid at 195 K, [c] Measurement done at 77 K

Conclusions and perspectives

Since the beginning of modern coordination chemistry and of photophysics, Cr(III) complexes have played an essential role in the development of these two correlated domains. 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 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 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 1, the so far reported chiral Cr(III) complexes are mainly restricted to discrete mononuclear complexes (entries 1-54). It would be of interest to study how chiral Cr(III) complexes behave in polynuclear structures (entries 55-58) or in more sophisticated assemblies where additional sources of chirality can be present (entries 59-61). Moreover, the kinetic inertness of Cr(III) complexes should allow the manipulation for their insertion into macromolecular matrices or platforms like polymers where other phenomenon like exciton-coupling or long-range chirality can enhance the chiroptical properties.

Acknowledgements

This work is supported through grants from the Swiss National Science Foundation (grant 200020\_178758).

**Keywords:** Chromium • Chiral • CPL • CD • NIR

[1] B. N. Samojlov, *J. Exp. Theor. Phys.* **1948**.

[2] a) C. A. Emeis, L. J. Oosterhoff, *Chem. Phys. Lett.* **1967**, *1*, 129-132; b) C. A. Emeis, L. J. Oosterhoff, *J. Chem. Phys.* **1971**, *54*, 4809-4819.

[3] a) L. E. MacKenzie, R. Pal, *Nat. Rev. Chem.* **2021**, *5*, 109-124; b) J. R. Brandt, F. Salerno, M. J. Fuchter, *Nat. Rev. Chem.* **2017**, *1*, 0045; c) D.-W. Zhang, M. Li, C.-F. Chen, *Chem. Soc. Rev.* **2020**, *49*, 1331-1343; d) F. Zinna, M. Pasini, F. Galeotti, C. Botta, L. Di Bari, U. Giovanella, *Adv. Funct. Mater.* **2017**, *27*, 1603719.

[4] a) K. Staszak, K. Wieszczycka, V. Marturano, B. Tylkowski, *Coordin. Chem. Rev.* **2019**, *397*, 76-90; b) R. Carr, N. H. Evans, D. Parker, *Chem. Soc. Rev.* **2012**, 7673-7686; c) M. C. Heffern, L. M. Matosziuk, T. J. Meade, *Chem. Rev.* **2014**, *114*, 4496-4539.

[5] a) E. S. Gauthier, L. Abella, N. Hellou, B. Darquié, E. Caytan, T. Roisnel, N. Vanthuyne, L. Favereau, M. Srebro-Hooper, J. A. G. Williams, J. Autschbach, J. Crassous, *Angew. Chem. Int. Ed.* **2020**, *59*, 8394-8400; b) N. Saleh, C. Shen, J. Crassous, *Chem. Sci.* **2014**, *5*, 3680-3694; c) L. Arrico, L. Di Bari, F. Zinna, *Chem. Eur. J.* **2021**, *27*, 2920-2934; d) H. Tanaka, Y. Inoue, T. Mori, *ChemPhotoChem* **2018**, *2*, 386-402; e) T. Mori, *Circularly Polarized Luminescence of Isolated Small Organic Molecules*, Springer, Singapore, **2020**.

[6] a) F. Zinna, L. Di Bari, *Chirality* **2015**, *27*, 1-13; b) B. Doistau, J.-R. Jiménez, C. Piguet, *Front. Chem.* **2020**, *8*, 555; c) M. Hasegawa, S. Sakurai, M. A. Yamaguchi, D. Iwasawa, N. Yajima, S. Ogata, Y. Inazuka, A. Ishii, K. Suzuki, *Photoch. Photobio. Sci.* **2020**, *19*, 1054-1062.

[7] a) G. Albano, G. Pescitelli, L. Di Bari, *Chem. Rev.* **2020**, *120*, 10145-10243; b) Y. Yang, K.-Z. Wang, D. Yan, *Chem. Commun.* **2017**, *53*, 7752-7755; c) J. Wade, J. R. Brandt, D. Reger, F. Zinna, K. Y. Amsharov, N. Jux, D. L. Andrews, M. J. Fuchter, *Angew. Chem. Int. Ed.* **2021**, *60*, 222-227; d) J. L. Han, P. F. Duan, X. G. Li, M. H. Liu, *J. Am. Chem. Soc.* **2017**, *139*, 9783-9786.

[8] J. L. Greenfield, J. Wade, J. R. Brandt, X. Shi, T. J. Penfold, M. J. Fuchter, *Chem. Sci.* **2021**, ***12***, 8589-8602.

[9] a) F. S. Richardson, *Chem. Rev.* **1979**, *79*, 17-42; b) F. S. Richardson, *Inorg. Chem.* **1980**, *19*, 2806-2812.

[10] J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki, G. Muller, *J. Am. Chem. Soc.* **2008**, *130*, 13814-13815.

[11] a) O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522-13533; b) L. A. Büldt, O. S. Wenger, *Chem. Sci.* **2017**, *8*, 7359-7367; c) C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057-1070.

[12] a) O. S. Wenger, *Chem. Eur. J.* **2019**, *25*, 6043-6052; b) O. S. Wenger, *Nat. Chem.* **2020**, *12*, 323-324; c) B. C. Paulus, K. C. Nielsen, C. R. Tichnell, M. C. Carey, J. K. McCusker, *J. Am. Chem. Soc.* **2021**, *143*, 8086-8098.

[13] T. H. Maiman, *Nature* **1960**, *187*, 493-494.

[14] a) D. T. Richens, *Chem. Rev.* **2005**, *105*, 1961-2002; b) L. Helm, A. E. Merbach, *Chem. Rev.* **2005**, *105*, 1923-1959.

[15] M. Cantuel, G. Bernardinelli, D. Imbert, J.-C. G. Bünzli, G. Hopfgartner, C. Piguet, *J. Chem. Soc. Dalton* **2002**, 1929-1940.

[16] a) J.-R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244-13252; b) C. Dee, F. Zinna, W. R. Kitzmann, G. Pescitelli, K. Heinze, L. Di Bari, M. Seitz, *Chem. Commun.* **2019**, 13078-13081.

[17] J.-A. Le Bel, *Bull. Soc. Chim. Fr.* **1874**, *22*, 337-347.

[18] J. H. Van't Hoff, *Arch. Neerl. Sci. Exactes Nat.* **1874**, *9*, 445-454.

[19] A. Werner, *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 121-130.

[20] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem. Int. Ed.* **1966**, *5*, 385-415.

[21] J. Gal, *Chirality* **2011**, *23*, 1-16.

[22] C. J. Hawkins, *Absolute configuration of metal complexes*, Wiley-Interscience, New York, **1971**.

[23] E. C. Constable, C. E. Housecroft, M. Neuburger, J. Schönle, J. A. Zampese, *Dalton Trans.* **2014**, *43*, 7227-7235.

[24] S. Treiling, C. F. Wang, C. Förster, F. Reichenauer, J. Kalmbach, P. Boden, J. P. Harris, L. Carrella, E. Rentschler, U. Resch-Genger, C. Reber, M. Seitz, M. Gerhards, K. Heinze, *Angew. Chem. Int. Ed.* **2019**, *58*, 18075-18085.

[25] Y. Sakabe, H. Ogura, *Inorg. Chim. Acta* **1991**, *189*, 225-228.

[26] P. Biscarini, M. Benedetti, R. Kuroda, F. Ferranti, *Eur. J. Inorg. Chem.* **2006**, *2006*, 3167-3176.

[27] R. D. Gillard, S. H. Laurie, D. C. Price, D. A. Phipps, C. F. Weick, *J. Chem. Soc. Dalton* **1974**, 1385-1396.

[28] S. Otto, M. Grabolle, C. Förtser, C. Kreitner, U. Resh-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, *54*, 11572-11576.

[29] J.-R. Jiménez, M. Poncet, S. Míguez-Lago, S. Grass, J. Lacour, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *Angew. Chem. Int. Ed.* **2021**, *60*.

[30] E. C. Constable, C. E. Housecroft, *Chemistry* **2020**, *2*, 759-776.

[31] A. Cotton, *J. Phys. Theor. Appl.* **1896**, *5*, 290-302.

[32] a) Y. Nagata, T. Nishikawa, M. Suginome, *Chem. Comm.* **2012**, *48*, 11193-11195; b) K. Noack, A. J. Thomson, *Helv. Chim. Acta* **1981**, *64*, 2383-2392.

[33] M. Cantuel, G. Bernardinelli, G. Muller, J. P. Riehl, C. Piguet, *Inorg. Chem.* **2004**, *43*, 1840-1849.

[34] J. E. Harris, N. Desai, K. E. Seaver, R. T. Watson, N. A. P. Kane-Maguire, J. F. Wheeler, *J. Chromatogr. A* **2001**, *919*, 427-436.

[35] S. Sharma, F. Lombeck, L. Eriksson, O. Johansson, *Chem. Eur. J.* **2010**, *16*, 7078-7081.

[36] M. Cortijo, C. Viala, T. Reynaldo, L. Favereau, I. Fabing, M. Srebro-Hooper, J. Autschbach, N. Ratel-Ramond, J. Crassous, J. Bonvoisin, *Inorg. Chem.* **2017**, *56*, 4555-4567.

[37] a) J. P. Riehl, F. S. Richardson, *Chem. Rev.* **1986**, *86*, 1-16; b) J. Autschbach, *Chirality* **2009**, *21*, E116-E152.

[38] S. Wada, Y. Kitagawa, T. Nakanishi, M. Gon, K. Tanaka, K. Fushimi, Y. Chujo, Y. Hasegawa, *Sci. Rep-UK* **2018**, *8*, 16395.

[39] a) R. Aoki, R. Toyoda, J. F. Kögel, R. Sakamoto, J. Kumar, Y. Kitagawa, K. Harano, T. Kawai, H. Nishihara, *J. Am. Chem. Soc.* **2017**, *139*, 16024-16027; b) M. Deng, N. F. M. Mukthar, N. D. Schley, G. Ung, *Angew. Chem. Int. Ed.* **2020**, *59*, 1228-1231; c) J. F. Kögel, S. Kusaka, R. Sakamoto, T. Iwashima, M. Tsuchiya, R. Toyoda, R. Matsuoka, T. Tsukamoto, J. Yuasa, Y. Kitagawa, T. Kawai, H. Nishihara, *Angew. Chem. Int. Ed.* **2016**, *55*, 1377-1381.

[40] J. Zhao, T. Zhang, X.-Y. Dong, M.-E. Sun, C. Zhang, X. Li, Y. S. Zhao, S.-Q. Zang, *J. Am. Chem. Soc.* **2019**, *141*, 15755-15760.

[41] S. Kaizaki, J. Hidaka, Y. Shimura, *Inorg. Chem.* **1973**, *12*, 142-150.

[42] T. Tsubomura, I. Ohkouchi, M. Morita, *B. Chem. Soc. Jpn.* **1991**, *64*, 2341-2348.

[43] M. Wang, J. England, T. Weyhermüller, S.-L. Kokatam, C. J. Pollock, S. DeBeer, J. Shen, G. P. A. Yap, K. H. Theopold, K. Wieghardt, *Inorg. Chem.* **2013**, *52*, 4472-4487.

[44] Y. Sakabe, H. Sakaguchi, H. Takayanagi, H. Ogura, Y. Iitaka, *Inorg. Chim. Acta* **1991**, *183*, 97-105.

[45] S. Kaizaki, J. Hidaka, Y. Shimura, *B. Chem. Soc. Jpn.* **1975**, *48*, 902-905.

[46] G. L. Hilmes, H. G. Brittain, F. S. Richardson, *Inorg. Chem.* **1977**, *16*, 528-533.

[47] A. Whuler, C. Brouty, P. Spinat, P. Herpin, *Acta Crystallogr. B* **1977**, *33*, 2877-2885.

[48] B. Doistau, G. Collet, E. Acuna Bolomey, V. Sadat-Noorbakhsh, C. Besnard, C. Piguet, *Inorg. Chem.* **2018**, *57*, 14362-14373.

[49] S. J. Milder, J. S. Gold, D. S. Kliger, *Inorg. Chem.* **1990**, *29*, 2506-2511.

[50] A. Hauser, M. Mäder, W. T. Robinson, R. Murugesan, J. Ferguson, *Inorg. Chem.* **1987**, *26*, 1331-1338.

[51] J. N. van Niekerk, F. R. L. Schoening, *Acta Crystallogr.* **1952**, *5*, 196-202.

[52] J. Fan, M. Seth, J. Autschbach, T. Ziegler, *Inorg. Chem.* **2008**, *47*, 11656-11668.

[53] N. Anzai, H. Kurihara, M. Sone, H. Furukawa, T. Watanabe, K. Horie, S. Kumar, *Liq. Cryst.* **2006**, *33*, 671-679.

[54] N. Anzai, S. Machida, K. Horie, *Chem. Lett.* **2001**, *30*, 888-889.

[55] N. Anzai, S. Machida, K. Horie, *Liq. Cryst.* **2003**, *30*, 359-366.

[56] X. Hua, K. Larsson, T. J. Neal, G. R. A. Wyllie, M. Shang, A. Graham Lappin, *Inorg. Chem. Commun.* **2001**, *4*, 635-639.

[57] M. Herren, H. Horikoshi, M. Morita, *Mol. Cryst. Liq. Crys. A* **1996**, *285*, 573-578.

[58] R. D. Peacock, B. Stewart, *J. Chem. Soc. Chem. Comm.* **1982**, 295-296.

[59] S. Kaizaki, M. Ito, *B. Chem. Soc. Jpn.* **1981**, *54*, 2499-2502.

[60] M. Benedetti, P. Biscarini, A. Brillante, E. Castrglioni, *Enantiomer* **1999**, *4*, 63-66.

[61] D. J. Radanović, M. I. Djuran, M. B. Dimitrijević, B. E. Douglas, *Inorg. Chim. Acta* **1991**, *186*, 13-19.

[62] a) S. Kaizaki, H. Mori, *B. Chem. Soc. Jpn.* **1981**, *54*, 3562-3565; b) D. J. Radanovic, B. E. Douglas, *J. Coord. Chem.* **1975**, *4*, 191-198.

[63] S. Kaizaki, J. Hidaka, Y. Shimura, *B. Chem. Soc. Jpn.* **1969**, *42*, 988-994.

[64] N. Koine, M. Iida, T. Sakai, N. Sakagami, S. Kaizaki, *J. Chem. Soc. Chem. Comm.* **1992**, 1714-1716.

[65] a) M. A. Subhan, T. Suzuki, S. Kaizaki, *J. Chem. Soc. Dalton* **2001**, 492-497; b) M. A. Subhan, T. Suzuki, S. Kaizaki, *J. Chem. Soc. Dalton* **2002**, 1416-1422.