A Method for Sensitive Linear Dichroism Analysis of Metal Complexes Dissolved and Oriented in Organic Polymers

BENGT NORDÉN and
ÅKE DAVIDSSON

Division of Inorganic Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

This report suggests as a spectroscopic method the study of the linear dichroism emerging from a chemical species dissolved in an oriented polymer when the molecules exhibit (a) anisodimensional shape and (b) optical anisotropy. If any two of the three factors, *molecular shape, direction of polarisation* of the studied transition and its *energy*, are known, information about the third can be obtained. With a sensitive detection, cases with almost spherical molecules, low optical anisotropy or diffuse energy position due to low intensity drowning in neighbouring bands, may be studied. The species so far studied with the linear dichroism (LD) technique with stretched films have been generally long organic molecules. The fact that we have been able to record the linear dichroism from low intensity transitions of rather small inorganic complexes shows how effective the method is.

The measurements are performed using *one circular dichroism spectrometer* supplemented with *a quarter wave modulator* in combination with *a polymer, with a well defined internal orientation*, which contains the specimen. The spectrometer should be of a type (Jouan, Cary, Jasco) using rapidly changing right and left circular polarisation and an electronically synchronised detection, and with a sensitivity of about 10^{-5} absorbance units. The modulator that we have introduced is a high quality polyethylene film free of birefringence. It is placed perpendicular to the incident light, followed by a sample exhibiting *circular dichroism* (CD). The film is stretched until the CD recorded has become exactly zero, at a wavelength range where linear dichroism is to be measured. Then the instrument will detect not circular dichroism but the absorbance difference, between light polarised $+45$ and $-45°$, respectively, from the direction of

stretch in the modulator,[1] looking down the light path towards the detector ($+$ = clock-wise). The CD probe sample is then removed. By inserting the stretched sample-film with the stretch direction at the $+45°$ position, the possible absorbance difference $A(\text{II}) - A(\underline{\mathsf{L}})$ will be detected; $A(\text{II})$ is the absorbance when the electric vector of light is parallel to the direction of orientation (= stretch).[2,3] As the phase lag in the modulator will be exactly $\lambda/4$, and not $(k+\frac{1}{4})\lambda, k \in N$, as in conventional quarter wave plates, the wavelength dependence will be at a minimum, at least for wavelengths far from the absorbance region of the modulator material. This, and the fact that the birefringence (stretch) can be changed after the wavelength to maintain a quarter wavelength phase lag, make the modulator very convenient as a linear dichroism accessory to a circular dichroism instrument.[4] For simplicity we have in this Linear Dichroism study adopted the symbol LD for $A(\text{II}) - A(\underline{\mathsf{L}})$, *with sign and in absorbance units*, in consequence with $CD = A(\text{left}) - A(\text{right})$.

Figs. 1 and 2 represent two classes of the studied metal complexes which are characterised by strong and weak LD/A ratios, due to a high and a low degree of orientation, respectively. Bis(acetyl-
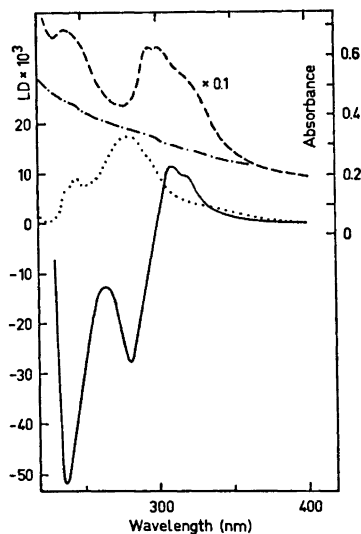

Fig. 1. Cu(acac)$_2$ absorbance $---$, LD$= A(\text{II}) - A(\underline{\mathsf{L}})$ ———, Cu(bipy)$_2$(ClO$_4$)$_2$ absorbance $- \cdot -$, LD $\cdots$, in polyethylene, R$=3.0$.
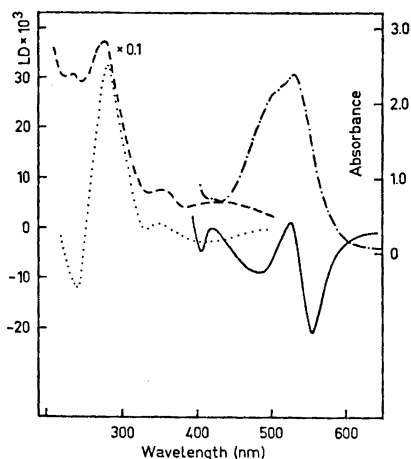
Fig. 2. Fe(acac)$_3$ in polyethylene, R = 3.0, absorbance — — —, LD ···; Fe(bipy)$_3$(ethylsulsulphate)$_2$ in polyvinylalcohol, R = 3.0, absorbance — · —, LD ———.

acetonato)Cu(II) and bis(2,2′-bipyridine)-Cu(II) perchlorate (Fig. 1) are typical planar monomeric [5-7] molecules. Their symmetry, D_{2h}, implies that any transition must be polarised along one of the orthogonal coordinate axes, x, y, or z (x connecting the centers of the ligands, z perpendicular to the molecular plane and through the metal nucleus). The number of the transitions and their polarisations of Cu(acac)$_2$ appear obvious: 4 transitions from 230 − 400 nm with pure y, y, x and x polarisation, respectively, if we assume that x is the long dimension of the molecule deciding the orientation. However, X-ray data show that the y dimension is comparable with that of x, *i.e.* the orienting effect must be derived from both x and y. Hence, the result is z, z, (x,y) and (x,y) polarised transitions, respectively.

In the case of Cu(bipy)$_2$$^{2+}$, the orientational contribution from the y-dimension is still more pronounced: The spectrum originates from $\pi \rightarrow \pi^*$ transitions which are known to be long-axis polarised in free bipyridine [2] and which should then have y-polarisation in Cu(bipy)$_2$$^{2+}$. As the spectrum indicates strong parallel polarisation, the y-dimension must have as good an orientating capacity as the x-dimension. It has been suggested[6] that the molecule is distorted from a strictly coplanar conforma-

tion due to steric hindrance by the hydrogens in the 3,3′ positions of the bipyridyl ligands. However, the fairly strong predominance of the y-polarisation cannot be explained if the internuclear bonds of the bipyridines were mutually tilted. On the other hand, with these bonds parallel and a bending around lines passing through the nitrogens on each ligand, the orientation effect due to the y-dimension should be even enhanced.

Other species which may belong to the 1st class are Ni(acac)$_2$ and Co(acac)$_2$. The considerably low LD/A (+ 0.3) value in the Ni case suggests a nonplanar structure with less polarisation and/or less orientation (tetrahedral, trimer[8]). The somewhat higher value in the Co case (+ 1.0) can be consistent with the theory of a tetramer[9] if acac is bridging in an octahedral (orientation giving positive LD for A_2 transition in D_3) or tetragonal configuration.

With Cu(propylenediamine)$_2$Cl$_2$ and Cu (prolinate)$_2$ which have been investigated in polyvinylalcohol (R = 3.0), positive LD values of the ligand field band indicate preferential x,y-polarisation. Max. LD/A = 0.05 (540 nm) and 0.06 (620 nm), respectively. Traces of a negative component at long wavelength in the first complex suggest a z-polarised contribution, probably $d_{z^2} \rightarrow d_{x^2-y^2}$. The very low LD/$A$, also on the short wavelength side, can be explained too by a z contribution, *viz.* d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$. With only $d_{xy} \rightarrow d_{x^2-y^2}$, the band should have been purely xy polarised, *i.e.* should have had LD/A of a higher magnitude. Another possible explanation is a decreased orientation due to axial ligands.

The second class (Fig. 2) consists of molecules which to a first approximation are spherical. Hence, they should not exhibit linear dichroism. However, in LD spectra on films with high concentrations of these species, strong effects were recorded, though LD/A was very low. With Fe(bipy)$_3$$^{2+}$, the effect was first believed to be due to orientation by outer-sphere complexation;[10] the effect was somewhat enhanced when replacing sulphate^{2-} with ethylsulphate$^-$. With Fe(phenantroline)$_3$$^{2+}$, a very similar LD spectrum was obtained, *viz.* from long to short wavelength: one negative and one weak positive band, respectively, corresponding to the low-energy transition, followed by a negative band. The first two bands should correspond to A_2 and E transitions in D_3. However, the indentification will not be clear until we know how the complex is oriented.

The theory of an outer sphere complex for orientation is ruled out by the observation that the neutral complexes $Fe(acac)_3$, $Co(acac)_3$, $Cr(acac)_3$ all exhibit fairly strong LD. A possible explanation in these cases seems to be trigonal distortions of the octahedral structures. With a complex compressed or elongated along the C_3-axis, orientation can be effectuated as for a disc or a rod, respectively. However, the extension of the ligands is the origin of a planar shape. Thus the following dihedral (D_3) complexes could be circumscribed by cylinders (cylinder axis parallel to C_3-axis) with diameter/thickness ratios considerably larger than unity (given in parenthesis, estimated from X-ray data): $Co(en)_3^{3+}$ (2.72), $Fe(dipy)_3^{2+}$ (1.85), $Fe(phen)_3^{2+}$ (1.85), $Fe(acac)_3$ (1.88). *This means disc-like shapes with the plane perpendicular to the C_3-axis.*

In the absorption spectrum of $Fe(acac)_3$, the 280 nm band of free acac is important. The LD spectrum yields two bands with opposite signs as expected for the A_2 and E components that should arise [11] from the long-axis polarised transition in the free ligand. If the A_2 band is the positive one, the orientation is along the C_3-axis, *i.e.* the complex is elongated in this direction, and if E is positive it is compressed. According to *exiton theory* the E transition should occur at lowest energy, *i.e.* the last mentioned orientation should be the case (Fig. 2). This is also in harmony with the estimation of the diam./thickness ratio.

Although the present technique is in the early stages of development, we have already found that there are several possible useful applications besides the ordinary use of linear dichroism, *i.e.* for determination of directions of polarisation:

1. Via transitions with established polarisation, conclusions can be made about the molecular structure of a species containing the transitions.[2]

2. LD spectrum is often more differentiated, with possible positive and negative extrema, than ordinary absorption spectrum and is therefore also more suited for qualitative chemical analyses.

3. Strongly dichroic species can be more easily detected with LD than from absorbance. With $LD/A = 2$, the theoretical

upper limit, the sensitivity of the detection will be as many times higher as the sensitivity of the CD instrument is higher than that of the absorption spectrophotometer, *i.e. ca.* $100-1000$ times. We have actually found that pseudoisocyanin-N,N'-diethyl iodide can be detected in this way with a precision 100 times higher than at absorbance measurements, due to long-axis polarised $\pi \rightarrow \pi^*$ transitions.

As a special form of the first mentioned purely spectroscopical application, we may note the possibility of tracing low intensity transitions when they are hidden among transitions of opposite polarisation. This was recently demonstrated in our laboratory by the detection of a hidden $n \rightarrow \pi^*$ transition perpendicularly polarised to the plane of the tetraphenylporphyrin molecule.[12]

The sample handling has in principle been described elsewhere.[1-3] More details will be given later.[4,12,13]

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