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Geometries of Non-Transition-Metal Complexes of a Novel Chiral β-Keto Amide Tripodal Ligand Elucidated from the Optical Transitions to Excitonic States

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A novel chiral tripodal ligand (**1**) that forms complexes of high configurational purity with group 13 M^{3+} and ferric ions has been prepared. The ligand is built from a symmetrical trifunctional amine as an anchor, extended with chiral (L) amino acids as bridges, and terminated with β-keto amide groups as binding sites. The chirality embedded in each of the tripodal arms causes the two coordination isomers to become diastereoisomeric. Upon complexation with Al^{3+}, Ga^{3+}, In^{3+}, and Fe^{3+}, the Λ-cis isomer is preferentially formed. The optical absorption and circular dichroism spectra of the complexes show two new transitions that arise from exciton coupling among the three enolized keto amide ligands. From the energy differences between these two transitions and their oscillator and rotational strengths, we deduced that the metal ions are octahedrally coordinated to the tripodal ligand. Small distortions of the ligand geometry in each complex are reflected in the bands' relative intensities. A difference between the mode of Fe^{3+} ligation and those of the other metal ions is reflected in Lorentzian versus Gaussian spectral line shapes.

Introduction

Little is known about the configuration and chirality of group 13 metal complexes in solution, and no systematic attempt has so far been recorded to apply CD spectroscopy to these complexes.[1] This is possibly due to the lack of suitable models for such studies. Metal complexes such as aluminum tris(β-diketonates) are stereochemically nonrigid.[2] They racemize almost instantaneously at room temperature[3] and thereby greatly handicap any detailed spectral analysis. A way to overcome this difficulty is offered by the use of chiral ligands that are attached to a common anchor. This arrangement precludes the formation of the trans isomer while the presence of chiral centers renders the left- and right-handed coordination isomers diastereomeric and energetically nonequivalent and thereby nonequally populated at equilibrium conditions. Under optimal conditions, one of the diastereomeric complexes might even be formed exclusively. This would allow detailed spectral examination of a specific coordination isomer in spite of its kinetic lability.

In this article we describe the synthesis and properties of a novel chiral keto amide ligand that forms complexes of defined chiral sense when binding group 13 and ferric metal ions and report on the successful correlation of the UV and CD spectra of these complexes with their coordination geometry. We further deduce the mobility of the metal ions within the coordination cavity by fitting their absorptions to either Gaussian or Lorentzian curves.

The chiral β-keto amide binder is a C_3-symmetric, tripodal molecule that is assembled from a triamine as anchor, chiral amino acids as bridges, and terminating β-keto amide binding sites. This design relies on the structures of previously synthesized chiral C_3-symmetric tris(catecholate)[4] and tris(hydroxamate)[5] binders that proved to form Fe^{3+} complexes of defined helicity. The spectral analysis of these complexes is based on a model where the guest ions force the binding sites into a well-defined mutual orientation, allowing specific interactions between chromophores to take place. These interactions cause exciton coupling, the multiplicity and size of which reflect the coordination geometry and absolute configuration of the formed complex.

Results and Discussion

Synthesis, Solution Conformation, and Ion-Binding Properties. The synthesis of the tripodal ligand **1** is given in Figure 1. Acetoacetylation of L-leucine with diketene was performed according to a general procedure.[6] The N-protected amino acid was then activated by using *N*-hydroxysuccinimide (NHS)[7] and dicyclohexylcarbodiimide (DCC), followed by condensation with tris(2-aminoethyl)amine (Tren). Ligand **1** was isolated in 58% yield by flash chromatography. The single-chain analogue **2** was prepared according to the same procedure by replacing Tren with *n*-propylamine.

Table I. UV and CD Data for **1**–Metal Complexes[a]

M^{3+}	λ_{max}, nm	$10^{-4}\epsilon$, M^{-1} cm^{-1}	λ_{ext}, nm ($\Delta\epsilon$, M^{-1} cm^{-1})	$\Delta\epsilon^-/\Delta\epsilon^+$	$\Delta E/\epsilon^b$
Fe	254	4.6	248 (−132), 257 (0), 267 (+145)	0.91	0.0060
	255	4.4	248 (−127), 258 (0), 268 (+145)	0.88	0.0062
Al	264	4.4	256 (−249), 266 (0), 278 (+307)	0.81	0.0126
	264	3.0	256 (−136), 265 (0), 279 (+168)	0.81	0.0101
Ga	264	4.4	257 (−250), 267 (0), 280 (+289)	0.87	0.0123
	264	4.0	257 (−218), 268 (0), 280 (+252)	0.87	0.0118
In	266	4.7	259 (−252), 270 (0), 282 (+288)	0.88	0.0115
	267	3.3	258 (−177), 269 (0), 282 (+199)	0.89	0.0114

[a] Metal complexes of ligand **1** in methanol, 2.0×10^{-5} M (containing 1×10^{-2} M sodium acetate). Data from two independent experiments are given, indicating the possible inaccuracy due to incomplete complexation. [b] $\Delta E = \Delta\epsilon^+ - \Delta\epsilon^-$.

Examination of the ^1H NMR spectrum of **1** in $CDCl_3$ (Figure 2) shows that all its diastereotopic methylene protons are highly nonequivalent, suggesting high restriction of conformational freedom. This high anisotropy collapses in polar solvents (e.g. CD_3OD, DMSO-d_6). The origin of this phenomenon can be elucidated from comparison with single-chain model compounds, such as **2**, and previously studied systems.[4,5,8] The lack of the high anisotropy in the ^1H NMR spectrum of **2** (Figure 2, top) suggests *interchain* interactions as the cause for the high anisotropy

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(1) This is in contrast to a vast amount of literature concerning chiral transition-metal complexes. For example: (a) Dunlop, J. H.; Gillard, R. D. *Adv. Inorg. Chem. Radiochem.* **1966**, *9*, 185–215. (b) Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266–273. (c) Gillard, R. D.; Mitchell, P. R. *Struct. Bonding (Berlin)* **1970**, *7*, 46–86. (d) Saito, Y. *Top. Stereochem.* **1978**, *10*, 96–174. (e) Richardson, F. S. *Chem. Rev.* **1979**, *79*, 17–36. (f) Peacock, R. D.; Stewart, B. *Coord. Chem. Rev.* **1982**, *46*, 129–157.

(2) Carty, A. J.; Cragg, R. H.; Smith, J. D.; Toogood, G. E. *Annu. Rep. Prog. Chem., Sect. A: Phys. Inorg. Chem.* **1976**, *73*, 138–139.

(3) Okamoto, Y.; Yashima, E.; Hatada, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1051–1052.

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(5) Tor, Y.; Libman, J.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 6518–6519.

(6) Di Bello, C.; Filira, F.; Giormani, V.; D'Angeli, F. *J. Chem. Soc. C* **1969**, 350–352.

(7) Abbreviations: CD, circular dichroism; D μ_B, debye Bohr magneton; DCC, dicyclohexylcarbodiimide; DMAP, 4-(dimethylamino)pyridine; DMSO, dimethyl sulfoxide; FAB MS, fast atom bombardment mass spectrum; NHS, *N*-hydroxysuccinimide; THF, tetrahydrofuran; Tren, tris(2-aminoethyl)amine.

(8) Tor, Y.; Libman, J.; Shanzer, A.; Felder, C. E.; Lifson, S. *J. Chem. Soc., Chem. Commun.* **1987**, 749–750.

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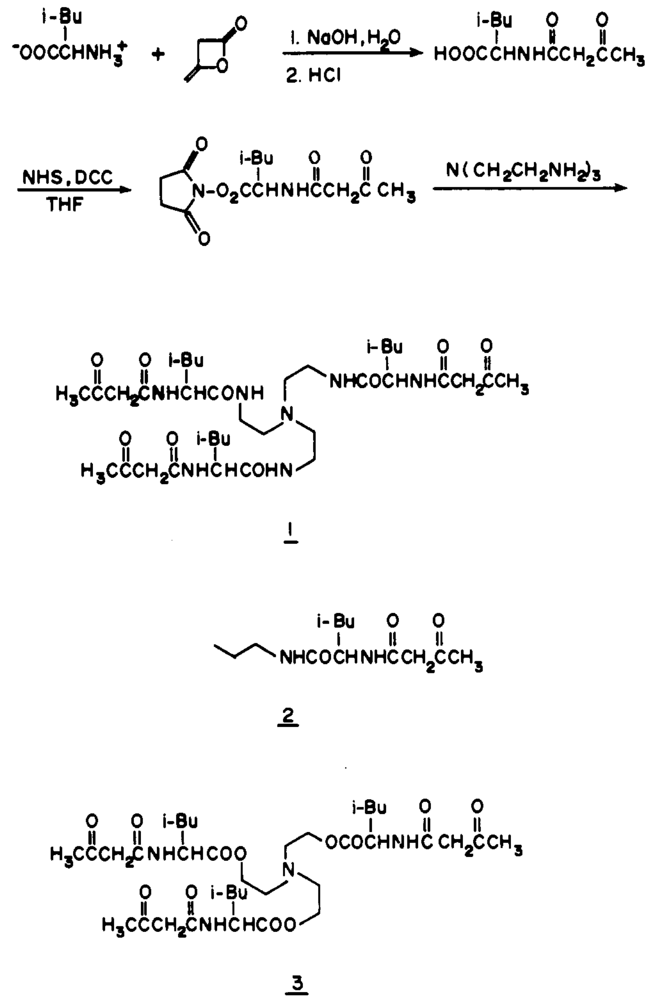

Figure 1. Synthesis of ligand 1 from Tren and *N*-(acetoacetyl)-L-leucine and the structural formula of its single-chain analogue 2 and its triester analogue 3.

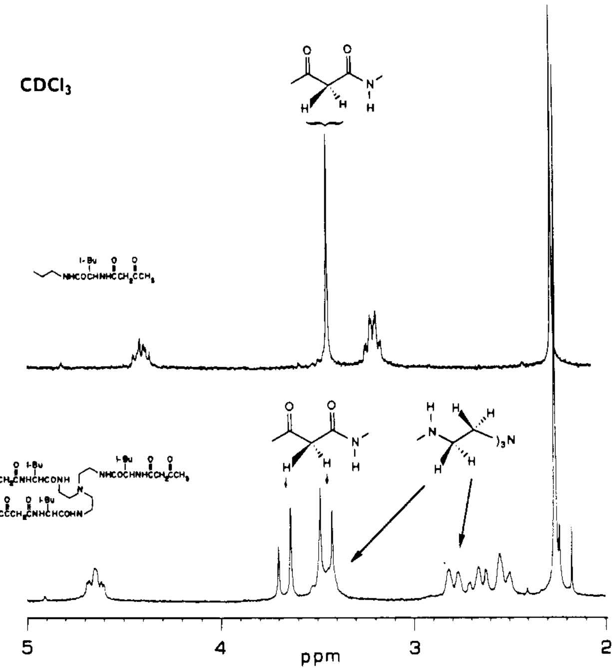

Figure 2. ^{1}H NMR spectra (270 MHz, CDCl$_3$) of the tripodal ligand 1 (bottom) and its single-chain analogue 2 (top), showing the high anisotropy of the diastereotopic methylene protons of 1.

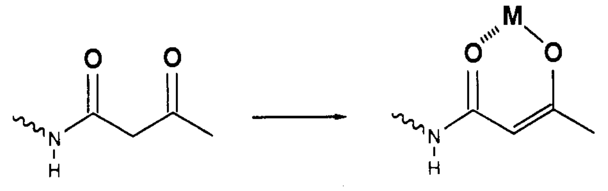

Figure 3. Schematic representation of the β-keto amide group emphasizing the atoms involved in metal coordination.

in 1. Moreover, comparison of temperature and solvent (DMSO-d_6) effects on the NH's chemical shifts reveals different behaviors for tripodal 1 and the single-chain compound 2.[9] This leads to the conclusion that a special type of interaction characterizes the tripodal compound. The infrared spectrum of a dilute CDCl$_3$ solution (2.5×10^{-4} M) shows NH frequencies at 3356 and 3288 cm^{-1}, thus suggesting hydrogen bonding as the cause for the conformational restriction. This type of *interchain* H-bonding ("circular H-bonding"[8]) causes the molecule to adopt a propeller-type structure of either right- or left-handedness.[8]

The complexation process of the ligand is monitored by following the enolate chromophore absorption around 260 nm (Table I, Figures 3 and 4). Titration of ligand 1 with M^{3+} ions (e.g. Al, Ga, In, Fe) proves the formation of 1:1 complexes with a half-lifetime of ca. 5 min for Ga^{3+} (2×10^{-5} M in CH$_3$OH, containing 1×10^{-2} M CH$_3$COONa, 30 °C). We attribute this relatively low time constant to the predominance of the keto tautomer, caused by the low acidity of the β-keto amide group.[10]

CD spectra of the equilibrated complexes' solutions showed very strong Cotton effects (see Table I, Figure 4, and discussion below) that are indicative of the preferential formation of the Λ-cis configurational isomer.[1d] Comparison of the anisotropy ratio ($\Delta\epsilon/\epsilon$) of 1-Al^{3+} to that reported for chiral HPLC-isolated Λ-Al(acac)$_3$[3] further supports this conclusion. Examination of the CD spectra of metal complexes of the triester ligand 3, lacking the anchor amide bonds, showed relatively weak Cotton effects (ca. 10% compared to 1). On the basis of these considerations, we suggest that H-bonds play a crucial role in stabilizing the preferred conformation of the metal complexes.

Spectral Properties of Metal Complexes. Figure 4 (left panel) illustrates the optical absorption spectra of Al^{3+}, Ga^{3+}, and Fe^{3+} complexes of 1 in the UV region. Each spectrum is composed of a major transition and a shoulder at a slightly longer wavelength and can be fitted with a background component and two Gaussian curves (for the Ga^{3+} and Al^{3+} complexes)[11] or by a background component and one Lorentzian curves (for the Fe^{3+} complex). The corresponding CD spectra (Figure 4, right) show a conservative double Cotton effect that can be fitted by two components only. These components are Gaussian curves for the Ga^{3+} and Al^{3+} complexes but Lorentzian curves for the Fe^{3+} complex. The peak locations of the CD components are slightly shifted relative to the peak locations of the corresponding absorption bands but the bands' separations are similar. Wavelengths for maximum absorption, λ_{max}, the corresponding molar absorption extinction coefficients, ϵ, and the molar dichroic absorbance, $\Delta\epsilon$ (defined as the difference between the absorbances of left- and right-handed polarized light per mole) are summarized for each metal complex in Table I.

Enolization of similar β-diketones (e.g. acetylacetone) introduces a new band that has a maximum absorption at about 260–270 nm.[12] In a chiral environment (e.g., ternary complexes containing

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[9] Temperature coefficients: 1, C$_\alpha$NH- −0.0074 ppm/K, CH$_2$NH- −0.0013 ppm/K; 2, C$_\alpha$NH- −0.0036 ppm/K, CH$_2$NH- −0.0049 ppm/K. Solvent (DMSO-d_6) effect: 1, C$_\alpha$NH- 0.034 ppm/% DMSO, CH$_2$NH- 0.023 ppm/% DMSO; 2, C$_\alpha$NH- 0.22 ppm/% DMSO, CH$_2$NH- 0.26 ppm/% DMSO.

[10] The dominant form of the β-keto amide groups in CDCl$_3$ solution is the keto form, as revealed from the NMR spectrum. This is in agreement with other works: (a) Leyden, D. E.; Kendall, D. S.; Burggraf, L. W.; Pern, F. J.; DeBello, M. *Anal. Chem.* **1982**, *54*, 101–105. (b) Dietz, G.; Seshadri, T.; Haupt, H.-J.; Kettrup, A. *Fresenius' Z. Anal. Chem.* **1985**, *322*, 491–494.

[11] In^{3+} gave essentially the same optical and CD spectral patterns as Al^{3+} and Ga^{3+} (see Table I).

[12] Jaffe, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1965; pp 218–219.

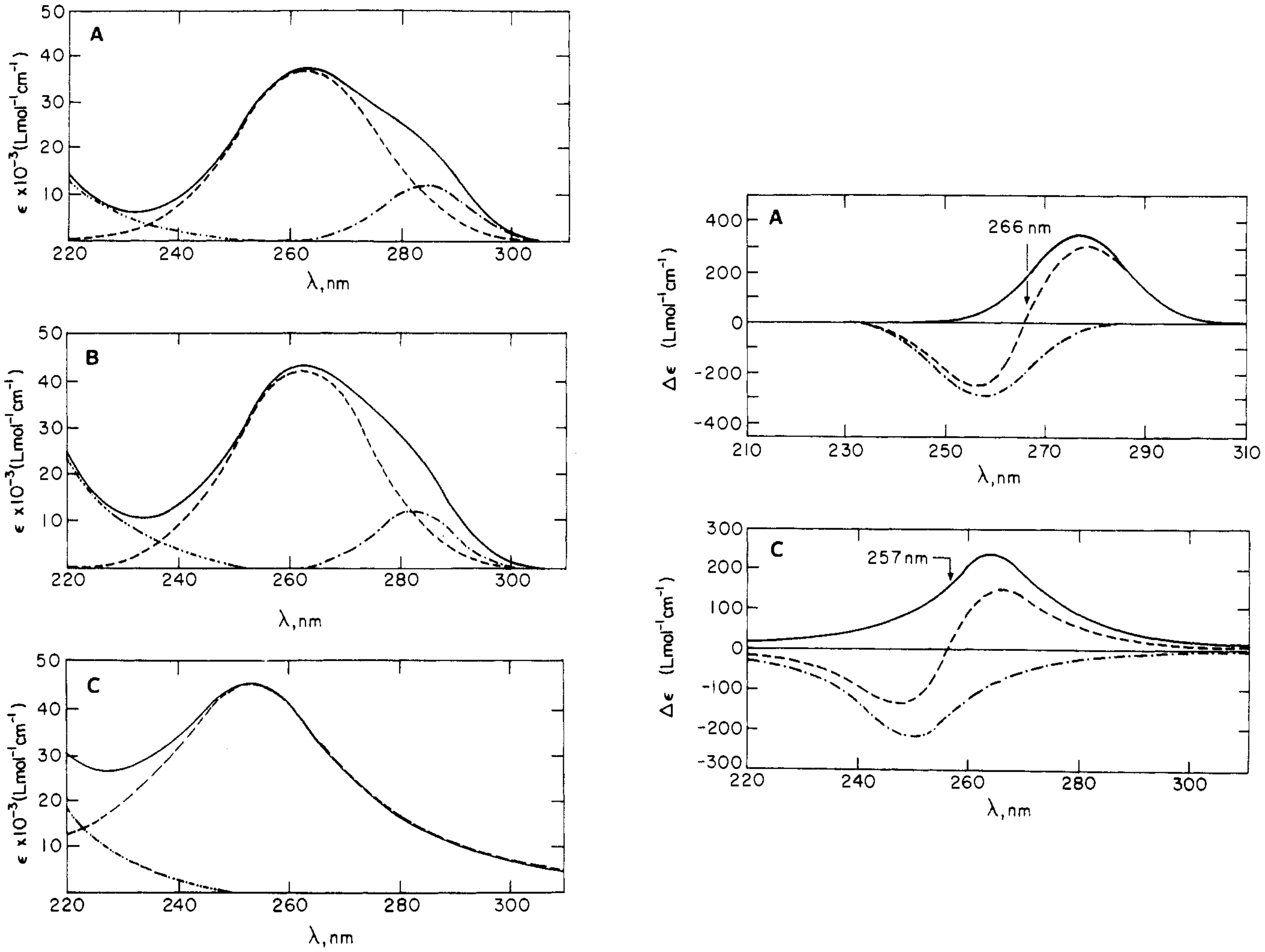

Figure 4. Optical absorption (left) and circular dichroism (right) spectra of M^{3+}-**1** complexes in methanol (2 × 10^{-5} M; 1 × 10^{-2} M sodium acetate): (A) Al^{3+}-**1**; (B) Ga^{3+}-**1**; (C) Fe^{3+}-**1**. Left: The solid lines stand for the experimental spectra. The dashed and the dashed–dotted lines designate the resolved exciton bands in each case. The dashed–double-dotted lines are background signals due to higher transitions.[11] Right: The dashed lines stand for the experimental spectra. The solid and the dashed–dotted lines designate the deconvoluted bands.

one enolate ligand), such a transition may be accompanied by a relatively weak single Cotton effect.[1b] The strong conservative and sigmoidal CD spectrum of the metal-bounded ligand **1** has been therefore taken as an indication of exciton coupling between the chromophores of the metalated tripods determined by the complex geometry. Since Gaussian line shapes usually reflect a rigid orientation of the excited chromophores whereas Lorentzian lines reflect rapid variations in the chromophores' environments,[13] the Fe^{3+} ion is probably more labile than a group 13 M^{3+} ion within the coordination cavity.

From simple model building we deduced that the chromophores in each of the metal complexes are separated by 4 Å or more from each other. Having a small chromophore size relative to their separation allowed us to calculate the exciton coupling in the point dipole approximation.[1b,14] The complexed system is characterized by the states ϕ_n, where ϕ_n are taken as linear combinations of the individual chromophore's states ψ_i ($\phi_n = \sum_i a_i \psi_i$) and the excitation energies are E_n. The interaction between each two transition dipoles is given by $V_{ij} = (1/R^3) \times (\bar{U}_i \bar{U}_j) - [(\bar{U}_i \bar{R}) \times (\bar{U}_j \bar{R})]/R^5{}_{ij}$ where $\bar{U}_i$ and $\bar{U}_j$ are the transition dipole vectors for the individual residues i and j, respectively, and $\bar{R}$ is the displacement of one dipole relative to the other, sitting at the origin of the coordinate system. Since the coupling of the ligand chromophores results in having only two transitions for each metalated ligand, as can be deduced from the Gaussian deconvolution of the CD and optical absorption spectra (Figure 4), two eigenstates of the complexed chromophores are degenerate.[1b,14] Hence, the transitions to the nondegenerate excitonic states are given by $E_1 = E + 2V$, $E_2 = E - V$, and $\Delta E = 3V$ ($V_{12} = V_{13} = V_{23} = V$). As the two bands in the UV region are separated by ≈2300 cm^{-1}, $V \approx 770$ cm^{-1}.

The total dipolar strength of the two excitonic transitions equals to approximately 44 D^2, meaning that the dipolar strengths of the individual transitions are about 14.3 D^2. Hence, the separation among the chromophores' centers should be 4.5 Å, assuming that they maintain an approximate C_3 symmetry.[1b]

Having the geometry of the transition dipoles, the rotational strength $\boldsymbol{R}$ was calculated to be ±11 D μ_B for the two excitonic transitions. These values are in a good agreement with the experimental values (±8 D μ_B).

Following Bosnich,[1b] the ratio between the dipolar strengths of the two transitions should be 2:1, where the higher energy transition is the stronger. However, in none of the examined complexes was this the case. In fact, the experimental ratio between the deconvoluted Gaussian curves is 6:1 for the Ga^{3+} and Al^{3+} complexes. This means that the ligand transition dipoles do not rest in the equatorial plane and are mutually rotated toward each other by about 145°. The absence of the lower energy exciton in the Fe^{3+} complex is more difficult to explain. It means that either the individual transition dipoles are close to being parallel to each other (±10°) or the lower energy excitonic transition mixes into charge-transfer states.[15]

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Conclusions

A novel chiral C_3-symmetric ligand built from a trifunctional amine as an anchor, extended with chiral amino acids, and terminated with β-keto amide ligands has been synthesized and studied. The free ligand adopts a chiral circularly organized conformation in apolar solvents due to interchain H-bonds ("circular H-bonds"). Upon complexation with group 13 M^{3+} and Fe^{3+} ions, complexes of high configurational purity are formed. The optical purity of these complexes is reflected in their strong CD signals, which can be simulated by a model based on the exciton approach. In this model, the three ligating chromophores provide a microenvironment with spectral properties that are strongly dependent on the nature of the bound metal ion. Interaction of the metal ions with the enolate residues is observed in the absorption line shapes, which reflect the rigidity of the metal in the ligand cavity (i.e., the Lorentzian line shape of the Fe^{3+} complex could result from the greater mobility of complexed Fe^{3+} ion in the cavity relative to Al^{3+} and Ga^{3+}). Having the transition dipoles oriented at $\approx 140°$ relative to each other, the three enolate groups should be organized in a counterclockwise manner, meaning that they retain a Λ-cis configuration. The sensitivity of the spectroscopic parameters to metal size and to deviations from ideal polyhedral geometry is under current investigation, as is their application to other ligating groups.

Experimental Section

Physical Methods. Electronic and circular dichroism (CD) spectra were measured by using a Hewlett Packard diode array spectrophotometer, Model 8450A, and a JASCO J-500C spectropolarimeter, respectively. The 270-MHz ^{1}H NMR spectra were obtained in various solvents, at 298 K, by using a Bruker WH-270 instrument. Tetramethylsilane (TMS) was used as internal reference. Infrared spectra were measured by using the Nicolet MX-1 FTIR spectrometer in a NaCl cavity cell.

Reagents. Commercially available starting materials and metal salts ($Fe(ClO_4)_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $GaCl_3$, $InCl_3$) were used with no further purification. Analytical grade solvents were dried and freed from stabilizers by passing them through a column of basic aluminum oxide.

***N*-(Acetoacetyl)-L-leucine.** L-Leucine (5.0 g, 38 mmol) was dissolved in aqueous sodium hydroxide solution (1.67 g, 42 mmol, 60 mL). The solution was cooled, and diketene (3 mL, 39 mmol) was added dropwise. After 6 h, the solution was first extracted with diethyl ether (3 × 30 mL) and acidified to pH 1-2 (aq HCl) and then extracted with ethyl acetate. The organic phase was washed with water, dried (Na_2SO_4), and concentrated to a small volume. The product (5.7 g, 70% yield) was obtained as a creamy white solid, mp 124-5 °C (lit.[16] 124-5 °C), by precipitation with *n*-hexane.

Tris((*N*-(acetoacetyl)leucinamido)ethyl)amine (1). A cold solution of *N*-(acetoacetyl)-L-leucine (1.075 g, 5 mmol) and NHS (0.63 g, 5.5 mmol) in THF (8 mL) was treated with DCC (1.14 g, 5.5 mmol, in 8 mL of THF). A catalytic amount of DMAP (18 mg, 0.15 mmol) was added, and the reaction mixture was kept overnight at 0-4 °C. The dicyclohexylurea was removed by filtration, and the resulting solution was treated with tris(2-aminoethyl)amine (0.24 mL, 1.6 mmol) under N_2 for 30 h. The THF was evaporated, and the residue was dissolved in chloroform (150 mL), extracted with water (3 × 30 mL), dried ($MgSO_4$), and evaporated. The product was isolated by flash chromatography[17] (6% $MeOH/CH_2Cl_2$) in 58% yield. Mp: 57-61 °C. Low-resolution FAB MS (methanol/glycerol): m/z 738 $[M + H]^+$. $[\alpha]^{29}{}_D$: -37.3 (*c* 0.15, MeOH). IR ($CDCl_3$, 0.25 mM): ν_{NH} 3356, 3288 cm^{-1}; $\nu_{C=O}$ 1719, 1673 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.71 (br d, 3 H, $C_\alpha NH$), 7.58 (br, 3 H, $CH_2N\mathit{H}$), 4.64 (m, 3 H, $C_\alpha H$), 3.69, 3.46 (ABq, 6 H, $COCH_2CO$), 3.45, 2.79 (split ABq, 6 H, $C\mathit{H}_2NH$), 2.66, 2.52 (split ABq, 6 H, NCH_2), 2.26 (s, 9 H, $COCH_3$), 1.7 (br m, 6 H, CH_2 (*i*-Bu)), 1.39 (m, 3 H, CH (*i*-Bu)), 0.94 (m, 18 H, CH_3 (*i*-Bu)).

(*N*-(Acetoacetyl)leucinamido)propane (2). *N*-(Acetoacetyl)-L-leucine (0.43 g, 2 mmol) was activated as described for **1** and treated with *n*-propylamine (0.16 mL, 2 mmol). The product was isolated in 52% yield by flash chromatography[17] (3% $MeOH/CH_2Cl_2$). IR ($CDCl_3$): $\nu_{C=O}$ 1715 ($COCH_3$), 1676 cm^{-1} (CONH). ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.91 (d, 1 H, $C_\alpha NH$), 6.27 (br, 1 H, $CH_2N\mathit{H}$), 4.40 (m, 1 H, $C_\alpha H$), 3.45 (s, 2 H, $COCH_2CO$), 3.21 (m, 2 H, $C\mathit{H}_2NH$), 2.27 (s, 3 H, $COCH_3$), 1.5-1.8 (m, 3 H, CH, CH_2 (*i*-Bu)), 0.92 (m, 6 H, CH_3 (*i*-Bu)).

Triester Ligand 3. A cold mixture of *N*-(acetoacetyl)-L-leucine (0.54 g, 2.5 mmol), triethanolamine (0.124 g, 0.83 mmol), and DMAP (0.3 g, 2.5 mmol) in 20 mL of chloroform was treated with DCC (0.57 g, 2.75 mmol, in 5 mL of chloroform). After 2 h at 0-4 °C, the reaction mixture was stirred at room temperature for an additional 30 h. The product (viscous oil) was isolated in 42% yield by flash chromatography[17] (3% $MeOH/CH_2Cl_2$). IR ($CHCl_3$): ν_{NH} 3428 (weak), 3341 cm^{-1}; $\nu_{C=O}$ 1738 (COO), 1716 (CH_2COCH_3), 1670 cm^{-1} (CONH). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.43 (m, 3 H, NH), 4.58 (m, 3 H, $C_\alpha H$), 4.15 (m, 6 H, CH_2O), 3.45 (s, 6 H, $COCH_2CO$), 2.83 (br t, 6 H, NCH_2), 2.28 (s, 9 H, $COCH_3$), 1.6 (br m, 9 H, CH and CH_2 (*i*-Bu)), 0.94 (m, 18 H, CH_3 (*i*-Bu)).

Metal Complexation. Methanolic stock solutions of the ligand and metal ions were prepared. Equivalent amounts were mixed, followed by the addition of 0.025 mL of 2 M aqueous sodium acetate (serving as a weak base). The final concentration of the complex was 2×10^{-5} M, containing 1×10^{-2} M sodium acetate.

Spectral Calculations. Convolution was carried out by using the CURFIT program of the Weizmann Institute of Science, with averaged experimental data. The goodness of fit, $\eta = \sum_n(\chi_{cal} - \chi_{exp})^2 n^{-1}$ is better than 1%, where n is the number of convoluted points, χ_{exp} is their experimental absorption or circular dichroism, and χ_{cal} are the calculated values. The experimental μ^2 is given by $9.18 \times 10^{-3}[9n/(n^2 + 2)^2] \int \epsilon(\nu) \nu^{-1} \, d\nu$ in debyes squared. The experimental rotational strength is given by $\boldsymbol{R} = 0.248[9n/(n^2 + 2)^2] \int \Delta\epsilon(\nu) \nu^{-1} \, d\nu$, where n is the solvent index of refraction and $\boldsymbol{R}$ is given in debye Bohr magnetons (D μ_B).

Acknowledgment. We thank the United States-Israel Binational Science Foundation for support of this work. A. Scherz is the incumbent of the Recanati Career Development Chair.

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