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Posted Date: 12 August 2024

doi: 10.20944/preprints202408.0855.v1

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Article

The First Homoleptic Geometrical *anti*-Zn Complex from an Unsymmetric Curcuminoid

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Abstract: Curcuminoids are widely studied due to their well-recognized therapeutic properties. These molecules are often derivatized with metals, rendering their corresponding homoleptic metal complexes. Numerous crystal structures of homoleptic symmetric curcuminoids with physiologically essential metals are known, although the literature lacks reports of homoleptic unsymmetric metal complexes of curcuminoids (or hemi-curcuminoids). Two unknowns must be solved when an unsymmetric curcuminoid ligand is reacted with a metal ion: a) the degree of coordination (ML_n) and b) the conformational nature (*syn* or *anti*) of the complex. Herein, we report the structure of the *anti*-isomer of the Zn complex of the hemi-curcuminoid 5-hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-3-one. While the NMR shows only one set of signals for this homoleptic complex, the unambiguous stereochemistry was established through single-crystal X-ray diffractometry, revealing a hexacoordinated ML₂ structure.

Keywords: Hemi-curcuminoids; curcuminoids; homoleptic zinc metal complex; unsymmetric zinc complex

1. Introduction

Curcumin, the main active metabolite [1] of the spice *Curcuma sp.*, has garnered scientific interest due to its potential in treatment of Alzheimer's disease. Its therapeutic properties as anti-cancer, antioxidant, and anti-inflammatory [2], offer a promising avenue for research in biochemistry and pharmacology. Structurally, curcumin's beta-diketone group is in equilibrium of two possible tautomers in solution (keto and enol [3]); it also comprises two α,β -unsaturated systems [4] and a chain of seven carbon atoms [5] flanked by two aromatic rings substituted with *para*-hydroxy (-OH) and *meta*-methoxy (-OCH₃) groups (see Figure 1).

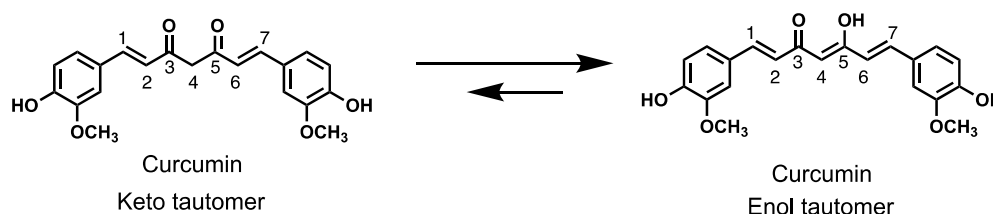


Figure 1. Curcumin structure.

The synthetic derivation of curcumin and the preparation of analogous compounds gives rise to different families of compounds called curcuminoids, such as diaryl-heptanoids [6], hemi-curcuminoids [7] (monoaryl-hexanoids), monocarbonyl curcuminoids [8,9] (diaryl-pentanoids) or half-curcuminoids [10] (monoaryl-propanoids) and are exemplified in Figure 2.

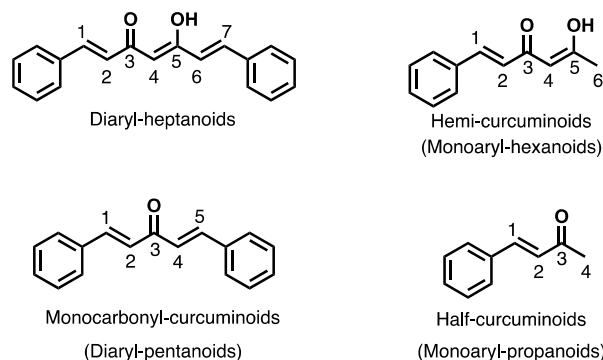


Figure 2. Families of curcuminoids.

After the derivatization of phenolic groups to methoxy or acetyl groups, the diarylheptanoids dimethoxy-curcumin and diacetyl curcumin (DAC) are obtained. However, when the double bonds are hydrogenated [11], the curcuminoids (e.g. tetrahydrocurcumin or hexahydrocurcumin) are obtained but still are considered part of the diarylheptanoid family.

It is important to note that curcuminoids are commonly derivatized with metals aiming to overcome inherent problems such as reduced aqueous solubility and low bioavailability [12,13]. Structural studies of curcuminoids with transition metals (e.g. Mg or Zn) have established stoichiometric ratios of 1:1 or 1:2. It is known that the two types of metal complexes that have been reported in the literature are homoleptic and heteroleptic complexes with symmetrical structural characteristics. Heteroleptic curcuminoid complexes [14] occur when complexation involves different ligands (e.g., bipyridines or phenanthrolines [15]), while homoleptic complexes arise when the same curcuminoid ligand occupies all the complexation sites (see Figure 3).

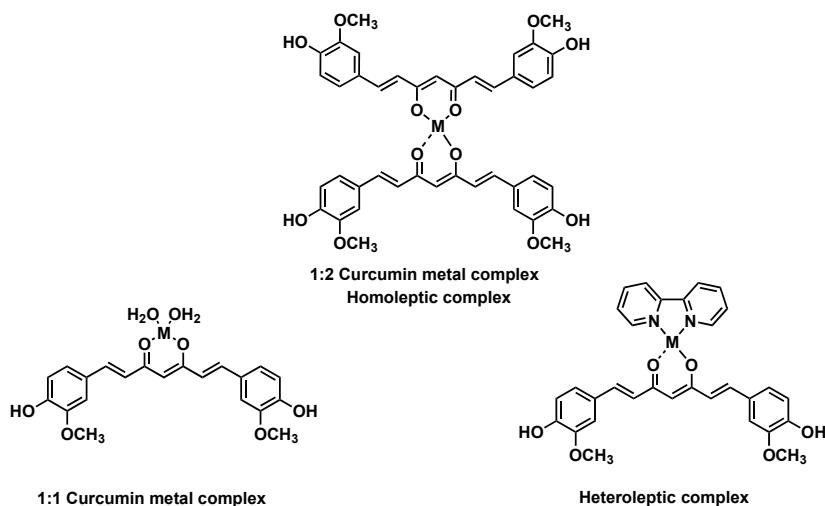


Figure 3. Type of metal complexes from curcumin, M= metal ion.

Analogue compounds inspired by the skeleton of curcumin [16] are named hemi-curcuminoids [17]. They can be obtained synthetically by preserving the skeleton's structural half, *i.e.*, an aromatic ring, the beta-diketone system, and the α,β -unsaturated function. A characteristic of this type of compound is its unsymmetrical nature [16], involving different molecular fragments at each side of the β -diketone function (see Figure 2). These compounds containing the β -diketone function can be readily deprotonated, giving rise to enolates capable of chelating with different metal ions. Although the metal coordination chemistry of the symmetric curcuminoid family has received much attention, the synthesis of unsymmetric curcuminoid metal complexes is unexplored with few examples in the literature [5]. In the latter case, the possible *syn* or *anti*-isomerism resulting from this new type of

metal complex must be assessed. In addition, unsymmetric curcuminoids are not readily available, and synthesis using the commonly described methods leads also to symmetric curcuminoids [18].

Zinc is an element involved in various biochemical processes [19] and is considered crucial in healthy metabolism. However, zinc metal curcuminoid complexes are biologically active against different cancer cell lines, and their physicochemical properties (e.g., aqueous solubility) exceed those of their parent curcuminoid ligands.

Zinc complexes are interesting in coordination chemistry due to their structural variety and diverse geometries [20] observed when a ligand (symmetric or unsymmetric) is reacted with such a metal ion. In addition, the degree of coordination (MLn) and the unambiguous geometry are best answered when established by X-ray of the single crystal technique. Several zinc homoleptic complexes of curcuminoids have been authenticated by single crystal studies [21,22], with the following geometries: square pyramidal, trigonal pyramidal, trigonal bipyramidal, or octahedral. In all these cases, symmetric curcuminoid ligands were used, and the solvent of crystallization plays an important role in defining the geometry, as shown in Figure 4.

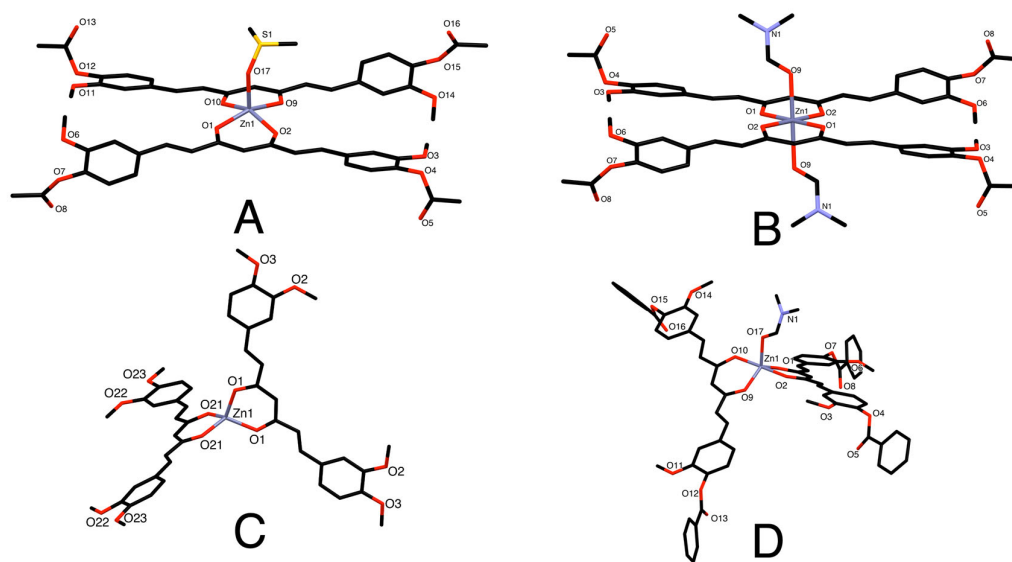


Figure 4. Several geometries of homoleptic zinc complexes, A: square pyramidal (CCDC 1453160), B: octahedral (CCDC 2234961) [22], C: trigonal pyramid (CCDC 2234962) and D: distorted trigonal-bipyramidal (CCDC 2234963), hydrogens have been omitted.

Herein, we report the preparation of an unsymmetric ligand (hemicurcuminoid type) using a new synthetic approach. Thus, a mono-ketalization reaction of 2,4-pentanedione with ethanediol, followed by the aldol mono condensation reaction with anisaldehyde in alkaline media, and further hydrolysis of the mono-ketal affords the target compound containing the beta diketone function.

Finally, the synthetic unsymmetric curcuminoid (5-hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-3-one) was reacted with zinc acetate and a suitable single crystal was obtained successfully by slow evaporation in methanol which provides three important structural features: a) metal-ligand relationship (MLn), b) coordination geometry, and c) the *syn* or *anti* isomerism (the latter being a new structural aspect for this type of complexes). All compounds were fully characterized using spectroscopic techniques.

2. Materials and Methods

Acetylacetone (acac, 2,4-pentanedione), ethanediol, *p*-toluenesulfonic acid, 4-methoxybenzaldehyde (anisaldehyde, CAS 123-11-5), zinc acetate, high-purity grade silica gel, average pore size 60 Å (52–73 Å), 70–230 mesh (CAS 112926-00-8), and all solvents HPLC grade were purchased from Sigma-Aldrich and were used without prior purification.

Melting points were obtained in an Electrothermal Engineering IA9100 digital melting point apparatus in open capillary tubes and were uncorrected [23]. ^1H , ^{13}C NMR spectra were obtained in a Bruker Fourier 400 MHz spectrometer using TMS as an internal reference and DMSO-d_6 or CDCl_3 as solvent. NMR spectra were processed with Mestre Nova software 12.0.3-21384 [24] and are found in the Supplementary Materials. IR absorption spectra were recorded using an FT-IR NICOLET IS-50, Thermo Fisher Scientific spectrophotometer in the range of $4000\text{--}400\text{ cm}^{-1}$ with a reflectance technique using an ATR diamond accessory [25]. Mass Spectra were recorded using The MStation JMS-700 JEOL equipment (Electron Ionization impact positive mode), the AccuTOF JMS-T100LC JEOL equipment (DART+, positive ion mode) and a Bruker Esquire 6000 equipment [26] (ESI-TI, APCI-TI).

Single-crystal X-ray Diffraction. The Rigaku Diffraction Xcalibur Atlas, Gemini CCD diffractometer was used for a single-crystal X-ray diffraction analysis of Compound **4**, with a graphite monochromator and $\text{MoK}\alpha$ source of radiation ($\lambda = 0.71073\text{ \AA}$) by a ω scan at 130K temperature. The collection and reduction of data were performed by the CrysAlis software package [27]. Crystal structure was solved using direct methods by SHELXS [28] and refined by the SHELXL [29] program. The structures were refined by the full-matrix least-squares method based on F^2 against all reflections. All non-hydrogen atoms were refined anisotropically. The hydrogen atom of the methanol ligand was found in the Fourier difference map, and its positional parameters were refined. The methoxy phenyl moiety is disordered and was modeled over two positions, with occupancies refined to about 0.5. Structures were visualized by MERCURY [30], and the geometrical parameters were calculated by PLATON [31]. The crystallographic data for **Compound 4** are summarized in Supplementary Materials.

Preparation of Compound 1 (Mono-ketal).

In a 250 mL round flask provided with a Dean-Stark apparatus, 5 mL of 2,4-pentanedione (50 mmol) was dissolved in 50 mL of benzene, then 1.4 mL of ethanediol (23 mmol) was added, after that 10 mg of *p*-toluenesulfonic acid monohydrate was added, and the reaction was left in reflux for 3 hours. Finally, after the removal of the solvent, the title product was purified by a reduced pressure distillation (50°C and 5 mm Hg).

Reaction of mono-condensation for obtained of compound 2.

In a 100 mL round flask, 1.7 mL of 4-methoxybenzaldehyde (14 mmol, anisaldehyde) was dissolved in 50 mL of methanol; then 2 g of compound **1** (12 mmol) dissolved in methanol was added dropwise. Later 0.5 g of NaOH (12.5 mmol) finely powdered was added to the vessel. The reaction was left with magnetic stirring at room temperature for 3 days. The solvent was evaporated in vacuo and an extraction with water (100 mL) and ethyl acetate (100 mL) 1:1 was carried out. The organic phase was dried with Na_2SO_4 and concentrated. The product was purified by SiO_2 column chromatography using a 6:4 hexane/ ethyl acetate mixture as eluent.

Synthesis of compound 3 (Unsymmetric hemicurcuminoid, enol type).

In a 100 mL round flask, 1.05 g of compound **2** was dissolved in 40 mL of methanol. Further, 2 mL of HCl (4.6 mmol) was added and the reaction was conducted with magnetic stirring at room temperature for 6 hours. The solvent was evaporated and the residue was extracted with a sodium bicarbonate saturated solution (50 mL) and ethyl acetate (50 mL) 1:1; the organic phase was dried with Na_2SO_4 and concentrated.

Synthesis of unsymmetric homoleptic complex and preparation of single crystal.

In a 100 mL round flask, 0.2 g of compound **3** was dissolved in 10 mL of ethyl acetate. Subsequently, 0.085 g of zinc acetate (4.6 mmol) dissolved in methanol were added dropwise. The reaction was left with magnetic stirring at room temperature for 3 hours and the precipitate was filtered off on a Hirsh funnel; the powder was washed with distilled water and dried in vacuum. 30 mg of the complex was dissolved in methanol and left standing for slow evaporation for 24 hours in the dark.

Compound 1. 1-(2-methyl-1,3-dioxolan-2-yl)propan-2-one, yield 60%. Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 3.98 (m, 4H), 2.78 (s, 2H), 2.22 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ

206.00, 107.82, 64.61, 52.52, 31.58, 24.37. IR-ATR 2985 cm^{-1} , 2886 cm^{-1} , 1707 cm^{-1} , 1183 cm^{-1} , 1047 cm^{-1} . DART⁺-MS: m/z = [M+H]⁺ 145.

Compound 2. Yield 40%. Oily brown liquid. (*E*)-4-(4-methoxyphenyl)-1-(2-methyl-1,3-dioxolan-2-yl)but-3-en-2-one. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 16.0 Hz, 1H), 7.51 (d, J = 8.7 Hz, 2H), 6.91 (m, 2H), 6.76 (d, J = 16.0 Hz, 1H), 3.98 (m, 4H), 3.84 (s, 3H), 2.98 (s, 2H), 1.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.85, 161.78, 143.07, 130.30, 127.41, 124.72, 114.54, 108.56, 64.88, 55.54, 50.64, 24.97. IR 1677 cm^{-1} , 1644 cm^{-1} , 1592 cm^{-1} , 1510 cm^{-1} . DART⁺-MS: m/z = [M+H]⁺ 263.

Compound 3. (*1E,4Z*)-5-hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-3-one. Yield 50%. Crystalline yellow solid. Melting point 68.5°C. ¹H NMR (400 MHz, CDCl₃) δ 15.48 (s, 1H), 7.55 (d, J = 15.8 Hz, 1H), 7.46 (m, 2H), 6.89 (m, 2H), 6.33 (d, J = 15.8 Hz, 1H), 5.61 (s, 1H), 3.83 (s, 3H), 2.14 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.15, 178.09, 161.29, 139.75, 129.69, 127.93, 120.51, 114.50, 100.86, 55.49, 26.95. IR-ATR 1629 cm^{-1} , 1282 cm^{-1} , 1109 cm^{-1} . IE⁺-MS: m/z = [M]⁺ 218.

Compound 4. Zinc Complex of 5-hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-3-one acetate. Yield 75%. Yellow powder. Melting point 94°C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.59 (m, 4H), 7.38 (d, J = 15.7 Hz, 2H), 6.95 (m, 4H), 6.59 (d, J = 15.7 Hz, 2H), 5.48 (s, 2H), 3.78 (s, 6H), 2.08 (s, 6H), 1.96 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 206.50, 193.27, 181.93, 160.21, 137.03, 129.31, 128.04, 127.00, 114.32, 100.63, 55.25, 30.68, 28.28. IR-ATR 1632 cm^{-1} , 1602 cm^{-1} , 1505 cm^{-1} , 450 cm^{-1} . ESI⁺-MS: m/z = 521.4 [M + Na]⁺.

3. Results

The production of a target hemi-curcuminoid compound (enol type) was achieved through the aldol mono-condensation reaction of 2,4-pentanedione (ACAC). Since there are two reactive terminal carbons at both ends susceptible to condensation, ACAC was functionalized blocking by ketalization one of the carbonyl groups with 1,2-ethanediol in an acidic medium (mono-ketal synthesis, see Figure 5). The structure of the mono-ketal from 2,4-pentanedione was determined spectroscopically. Thus, the proton magnetic resonance [32] (¹H NMR) showed multiple signals near 4 ppm assigned to the AA'BB' system corresponding to compound 1 (see Supplementary Materials). In addition, the mass spectrometry revealed a prominent peak at m/z = 145 for the molecular ion that corresponds adequately to the formula C₇H₁₂O₃.

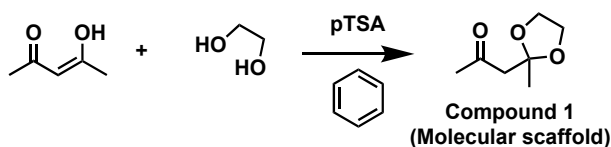


Figure 5. Preparation of mono-ketal from 2,4-pentanedione.

The adequate reactivity of the terminal methyl of compound 1 allows the aldol mono-condensation reaction with anisaldehyde in basic media (see Figure 6). The ¹H NMR signals of compound 2 showed two doublets at δ 7.54 ppm (b) and 6.76 ppm (a) assigned to the α,β -unsaturated vinyl system with coupling constants J = 16 Hz, correlating appropriately for the *trans* configuration. Additionally, the proton spectrum (see Supplementary Materials) showed multiple signals at δ 4 ppm due to the ketal group. The mass spectrum of compound 2 showed a peak at m/z = 263 [M+H]⁺ which corresponds to the molecular formula C₁₅H₁₈O₄.

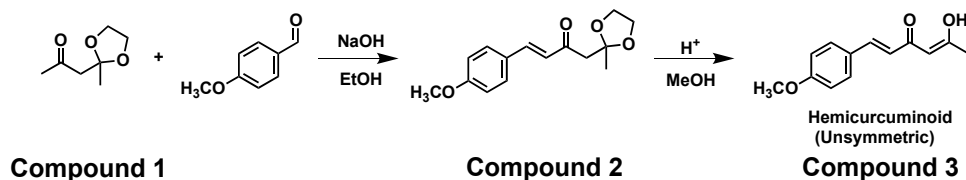


Figure 6. Synthesis of unsymmetric hemi-curcuminoid from anisaldehyde.

The opening of the mono-ketal (compound 2) in an acidic medium is illustrated in Figure 6 affording hemicurcuminoid 3 (recovery the keto-enol system). The ^1H NMR spectrum of compound 3 shows two simple signals characteristic of the enol, *i.e.*, the hydroxyl (-OH) was observed at 15.48 ppm (hydrogen bond) [33] and the methine (-CH-) at 5.61 ppm. In addition, the vinyl system characteristic for this compound is confirmed by the presence of two double signals at δ 7.55 ppm (β) and δ 6.33 ppm (α) with couplings *trans* J = 16 Hz [34] (see Supplementary Materials). Compound 3 has a molecular formula $\text{C}_{13}\text{H}_{14}\text{O}_3$ and was verified by a peak in the mass spectrum at m/z = 218 $[\text{M}]^+$, which is expected for the molecular ion.

In principle, the reaction of the hemicurcuminoid with zinc acetate can lead to two conformational isomers, *i.e.*, *syn* and *anti* as illustrated in Figure 7. The liquid state NMR data helped in the characterization of the complex but were not conclusive regarding the authentication of the molecular geometry. Therefore, the detailed single crystal X-ray analysis was imperative to answer this question.

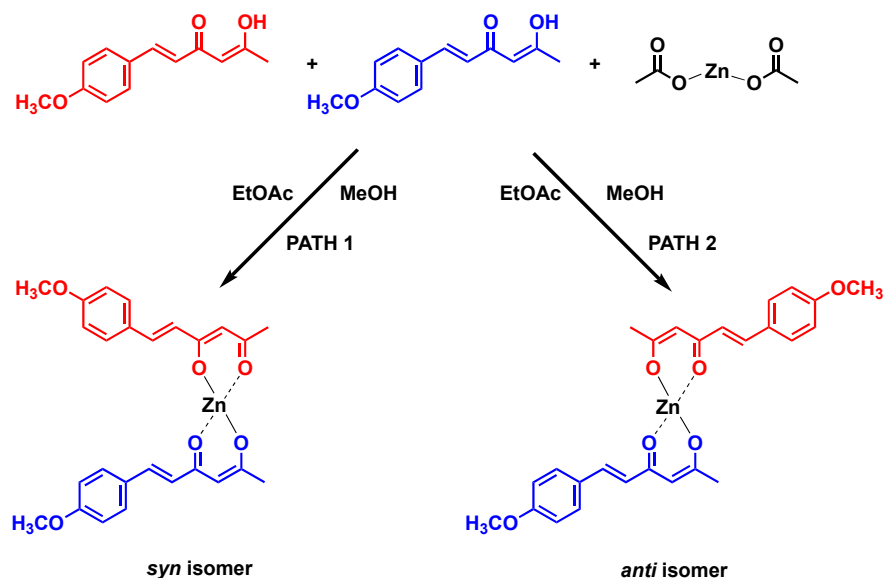


Figure 7. Synthesis of unsymmetric metal complex.

Proton magnetic resonance was indicative of the presence of the metal ion in the complex. When comparing the chemical shifts of the pure ligand with those of the zinc complex, a shift towards lower frequencies is observed [22] (Table 1). Surprisingly, compound 4 showed only one set of hydrogen and carbon-13 signals (see Supplementary Materials), which is indicative of the presence of a single isomer in solution ($\text{DMSO}-d_6$).

Table 1. Chemical Shifts of ligand (compound 3) and their zinc complex (compound 4).

Hydrogen	Compound 3, δ = ppm ¹	Compound 4, δ = ppm ¹
-CH ₃	2.13 (singlet)	1.96 (singlet)
=C-H (α)	6.66 (doublet)	6.59 (doublet)
=C-H (β)	7.54 (doublet)	7.38 (doublet)
-CH (Methine)	5.87 (singlet)	5.48 (singlet)
Ar-H (AA')	6.99 (multiplet)	6.95 (multiplet)
Ar-H (BB')	7.64 (multiplet)	7.59 (multiplet)
-O-CH ₃	3.80 (singlet)	3.78 (singlet)
-OH (enol)	15.65 (broad)	-
-OOC-CH ₃ (acetate)	-	2.08 (singlet)

¹ Solvent $\text{DMSO}-d_6$.

4. Discussion

The most desirable and common trend in the synthesis of curcuminoid-derived in the form of metal complexes is to find new biologically active compounds that respond to the needs of human ailments such as inflammation, cancer, and Alzheimer's disease. However, the architectural design of such relatively simple compounds may require an unambiguous structural determination before any biological testing is performed. In this order of ideas, the core of this research is to answer the structural unknowns of a new zinc complex (compound 4) that is obtained with an unsymmetric curcuminoid ligand.

The nuclear magnetic resonance spectrum for compound 4 showed signals corresponding to a single isomer and is the first time that a resonance spectrum of an unsymmetric curcuminoid ligand with zinc has been shown (see Figure 8 and Supplementary Materials). Finding a single set of NMR signals is unexpected because other zinc homoleptic complexes have shown two or more sets of NMR signals [35], thus the explanation will be in conjunction with X-rays. The NMR spectrum of compound 4 shows a singlet at 2.08 ppm (see Supplementary Materials) which corresponds to the acetate group coordinated with zinc. Upon crystallization of the crude precipitate in methanol, these acetate groups are replaced by methanol molecules as revealed by the x-ray crystal structure. Furthermore, the integration of signals normalized to two protons for the methine group ($-\text{CH}$ at 5.48 ppm) allowed us to propose an ML_2 -type hexacoordinated complex [22]. Although the geometry could not be unambiguously determined until the X-rays were available, the new complex of zinc was clearly of homoleptic type.

The work of Dawid Jędrzkiewicz *et.al.* [35], found that the zinc complex (L_2Zn) with an unsymmetric ligand (named O-dtBu, N-C12) produced more than one set of signals for the H-NMR spectrum which is attributed to a mixture of isomers in solution (*syn*-dimer and *anti*-dimer). The single set of signals observed in the proton spectrum of compound 4 in Figure 8, could correspond in principle to the *syn* or *anti*-isomer, but remarkably only one isomer is observed in solution.

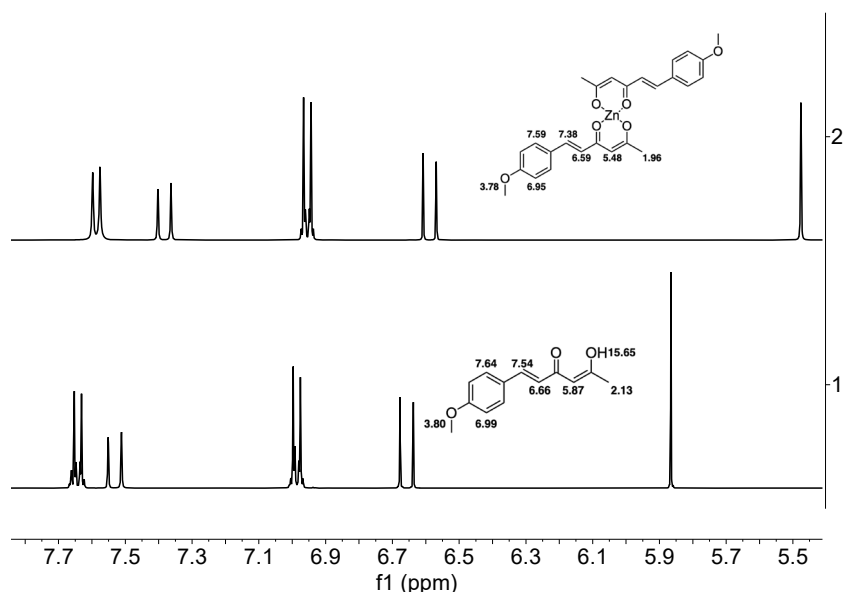


Figure 8. ¹H NMR spectra of hemicurcuminoid and their zinc complex (400 MHz, DMSO-*d*₆).

As it can be appreciated in Figure 9, both possible structures *syn* and *anti*, have the symmetry elements C_2 [36], and both would show a complete overlap of signals with possible differences in chemical shifts due to anisotropic effects from aromatic rings. Therefore, the optimal way to assess the geometry and configuration of the complex is X-ray crystallography.

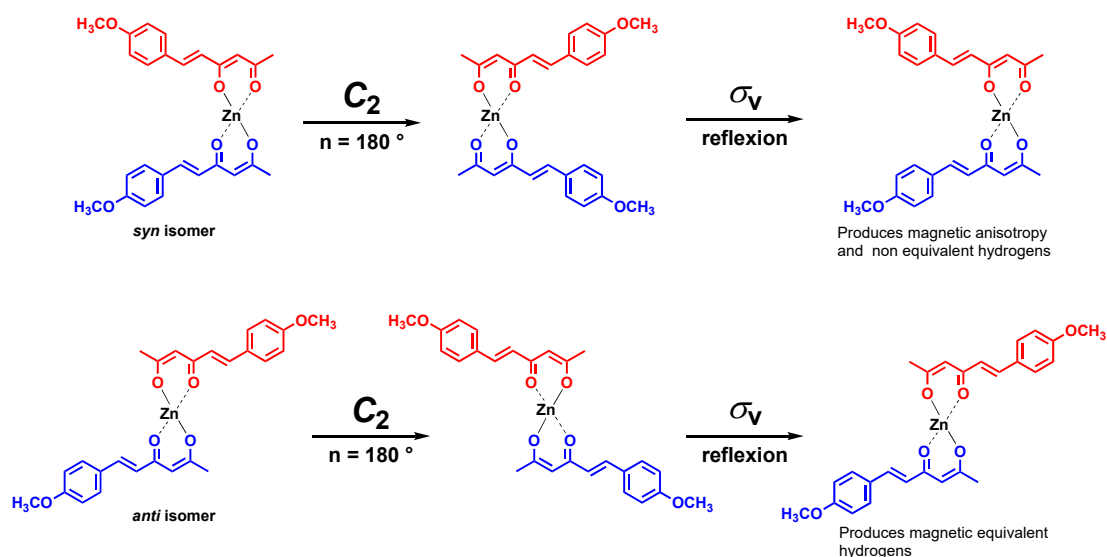


Figure 9. Symmetry operations for *syn* and *anti*-isomer complexes.

The *anti*-isomer too has the C_2 rotation axis with $n = 180^\circ$ and a symmetry plane (σ_v) that produces its reflection (shown in Figure 9), so these elements could explain the production of magnetically equivalent signals for each ligand around zinc. It is also interesting to note that an unsymmetric curcuminoid ligand produces magnetically equivalent signals when spatially arranged in the *anti*-form.

The synthesis and characterization of transition metal complexes of hemi-curcuminoids are scarce. There is only a couple of studies in which the monoaryl-hexanoids appear as a ligand in metal complexes [37,38], and a survey using the CSD (Version 5.45, update of June 2024) [39] revealed only three structure determinations (Ref Codes: JELZAF, JELZIN and JELZEJ) all of them for heteroleptic Ru(η^6 -*p*-cymene) complexes of three hispolon derivatives. To the best of our knowledge, this constitutes the synthesis and chemical characterization of the first homoleptic *anti*-Zn complex from an unsymmetric curcuminoid.

The asymmetric unit of compound **4** consists of one half of the neutral complex with th Zn having C_i symmetry lying on an inversion center, one deprotonated (1*E*,4*Z*)-5-hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-3-one molecule (Compound **3**) in the equatorial plane and one coordinated methanol molecule in apical position (Figure 10). The coordination geometry of compound **4** corresponds to a slightly apical distorted octahedron, presumed by Jahn–Teller effect, with zinc–oxygen from the coordinated methanol in apical/axial positions (2.201(3) longer than the equatorial zinc–oxygen bonds from the ligand (2.010(2)– 2.070(2) Å), all these values are slightly longer than zinc–oxygen bonds (equatorial: 1.986(3)–2.037(5) Å, axial 2.252(6) Å) of the close related compound **B** showed in Figure 4.

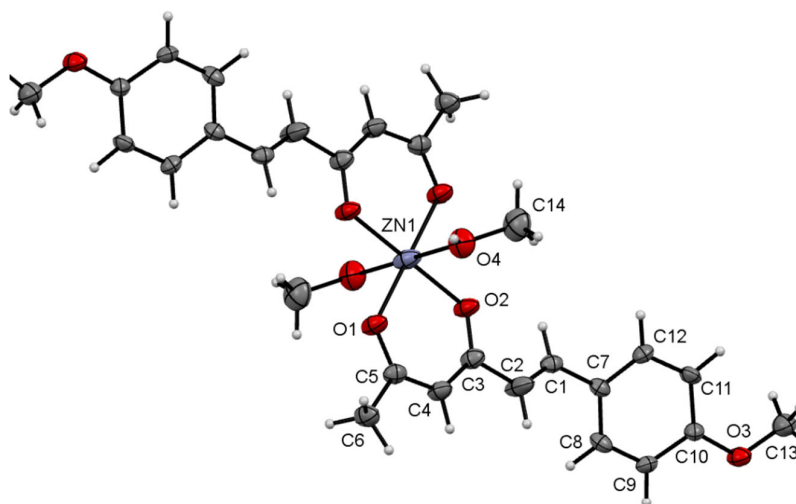


Figure 10. ORTEP-like drawing and coordination geometry of Compound **4**, 50% probability level of thermal ellipsoids, unlabeled atoms generated by inversion centre symmetry (minor disordered 4-methoxyphenyl atoms are omitted for clarity).

In the complex, the deprotonated (1*E*,4*Z*)-5-hydroxy-1-(4-methoxyphenyl)hexa-1,4-dien-3-one ligand displays a fully extended conformation with a significantly deviation of planarity. Two planes can be observed corresponding to the 5-hydroxy-hexa-1,4-dien-3-one moiety (Rms deviation = 0.0212 Å) and the 4-methoxyphenyl group (Rms deviation of fitted atoms = 0.0395 Å), making a dihedral angle of 28.85(0.18)°. A similar trend is observed in the heteroleptic Ru(η^6 -*p*-cymene) complexes of three hispolon derivatives (JELZAF: 28.01°, JELZIN: 14.32° and JELZEJ: 4.93°) revealing the high flexibility of this type of ligands. In the crystal complex molecules are held together by hydrogen bonds O4-H4A...O1(*x*-1, *y*, *z*): 2.10(5) Å, forming dimers, Figure 11.

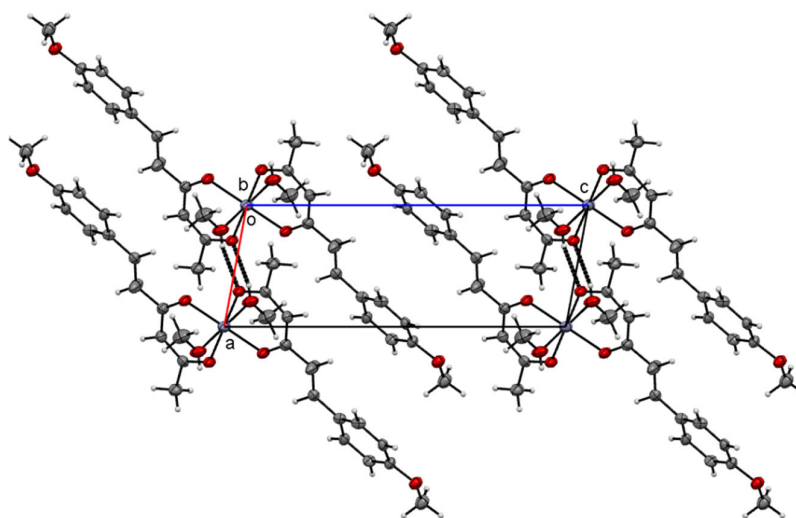


Figure 11. Crystal structure of Compound **4** along the *b*-axis. Hydrogen bonds represented by broken line.

5. Conclusions

This research has established the guidelines for a structural problem of isomerism in unsymmetric curcuminoid metal complexes. It is also crucial to recognize the value of complementary single-crystal X-ray structural analyses for curcuminoid-derived metal complexes. It is important to note that an apparent simple molecular design demands detailed structural studies before carrying out a series of biological assays.

To the best of our knowledge, this report constitutes the first crystal structure of a metal complex of an unsymmetric curcuminoid. Although the structure found has *anti*-configuration, it remains unknown if the *syn* configuration is also present at some stage of the complex formation. X-ray crystallography offered the most conclusive answer regarding the preferred geometry of the complex. A detailed study of the thermodynamics associated with the complex formation may provide insight into determining the selectivity of the preferred geometric isomer.

Supplementary Materials: The deposit number CCDC 2376717 (Compound 4) contains the supplementary crystallographic data for this article, including structure factors. These data can be obtained free of charge at <https://www.ccdc.cam.ac.uk/structures/> (accessed date 09 August 2024). The following supporting information can be downloaded at: www.mdpi.com/xxx/s1.

Author Contributions: Conceptualization, R.G.E.; methodology, M.A.O.M, G.M.E., R.T.H., R.S.O.; software, M.A.O.M, G.M.E., R.T.H., R.S.O., R.A.T.; validation, R.G.E, and R.A.T; formal analysis, M.A.O.M, G.M.E., R.T.H., R.S.O., R.A.T., R.G.E.; investigation, M.A.O.M, G.M.E., R.T.H., R.S.O.; resources, R.G.E.; data curation, R.G.E, and R.A.T.; writing—original draft preparation, R.G.E.; writing—review and editing, R.G.E.; visualization, R.G.E.; supervision, R.G.E.; project administration, R.G.E.; funding acquisition, R.G.E.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by CONAHCyT, grant number FOINS-PRONACES-307152 and PAPIIT DGAPA-UNAM, grant number IT200720.

Data Availability Statement: Not applicable.

Acknowledgments: Raúl G. Enríquez acknowledges support from CONAHCyT (FOINS-PRONACES-307152) and DGAPA-UNAM (IT200720). Marco A. Obregón-Mendoza acknowledges honorary payment from CONAHCyT (FOINS-PRONACES-307152). R.T.H. acknowledges CONAHCyT by the postdoctoral fellowship (CVU-662794) and G.M.E. CVU-1347017 to CONAHCyT scholarship. Acknowledgments are extended to Elizabeth Huerta (NMR), Isabel Chávez (NMR), Adriana Romo (IR), María del Carmen García (MS), Eréndira García Ríos (ESI) and Lucero Ríos (ESI) from Instituto de Química-UNAM.

Conflicts of Interest: The authors declare no conflicts of interest.

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