Articles

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Synthesis and Molecular Structure of the Eight-Coordinate Complex Bis(4-amino-N,N'-disalicylidene-1,2-phenylenediaminato)zirconium(IV), a New Reagent for Preparing Coordination Polymers

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The precursor complex bis(4-nitro-N,N'-disalicylidene-1,2-phenylenediaminato)zirconium(IV), Zr(ndsp)$_2$, was synthesized from the appropriate Schiff-base ligand and zirconium tetra-n-butoxide butanol complex (2:1, respectively) and then catalytically hydrogenated to produce the polymerizable diamine complex bis(4-amino-N,N'-disalicylidene-1,2-phenylenediaminato)zirconium(IV), Zr(adsp)$_2$. Both complexes were characterized by elemental analysis and IR, NMR, and UV–vis spectroscopy; the Zr(adsp)$_2$ complex was further characterized by X-ray crystallography as a trisolvate. The structure of the Zr(adsp)$_2$ complex was shown to consist of two perpendicularly disposed quadridentate ligands, similar to that of the unsubstituted complex, Zr(dsp)$_2$, and consistent with theoretical predictions. Other details of the crystallography include the following: formula C$_{40}$H$_{30}$N$_6$O$_4$Zr·DMF·1.5C$_6$H$_5$CH$_3$, space group $P\bar{1}$, with a = 12.006 (2) Å, b = 14.023 (2) Å, c = 14.517 (3) Å, α = 94.15 (1)°, β = 103.26 (1)°, γ = 99.15 (1)°, V = 2333.7 Å^3, Z = 2, and D(calcd) = 1.372 g cm^{-3}. Refinement of 600 variables using 4811 observations converged at R = 5.65%. Preliminary viscosity results on products obtained from reactions between Zr(adsp)$_2$ and pyromellitic dianhydride or terephthaloyl chloride indicate that soluble (DMF, DMSO, NMP) oligomers are produced.

Introduction

Polyamide and polyimide polymers have been utilized in many important ways as a result of their excellent high-temperature stability (including thermooxidative stability), electrical properties, and mechanical strength. However, the wholly aromatic varieties of these polymers, which display the greatest high-temperature stability, suffer from two serious limitations. (1) Due to the very high softening temperature (T_g) of these materials, processing via a hot melt technique—such as melt spinning or injection molding—is rendered impractical. (2) Certain synthetic difficulties also remain: (a) If polyimides are prepared from polyamic acids, the rigidity of the wholly aromatic chemical structure interferes with complete cyclization; also, the elimination of water during cyclization causes "voids" in thickly laminated composites or compression molds. (b) If the rigid aromatic imide or amide structure is incorporated into the monomer, the low solubilities of the oligomers can prevent high degrees of polymerization.

Numerous attempts to address these limitations have been reported in the recent literature.[1] Variables that have been investigated include incorporation of heteroatoms or heteroatomic groups or noncoplanar biphenyl groups into the polymer chain,[1a] block, random, or regular copolymerization,[1b–h] N-alkylation or N-arylation of polyamides,[1i] and aromatic ring isomer effects.[1g,h,j]

Incorporation of chelated metal complexes that contain two free amino groups into a polymer chain represents still another attempt to diminish the strength of the interaction between rigid polymer chains, thus lowering the T_g and improving solubility properties without serious loss of high-temperature stability. Therefore, we wish to report the synthesis, molecular structure, and some preliminary polymerization behavior of the eight-coordinate diamine complex bis(4-amino-N,N'-disalicylidene-1,2-phenylenediaminato)zirconium(IV), Zr(adsp)$_2$.

Experimental Section

The 4-nitro-o-phenylenediamine (Eastman Kodak or Aldrich), salicylaldehyde (Aldrich), and zirconium n-butoxide butanol complex (Alfa Products) reagents were used without purification, and their identities

H$_2$ndsp   Zr(adsp)$_2$
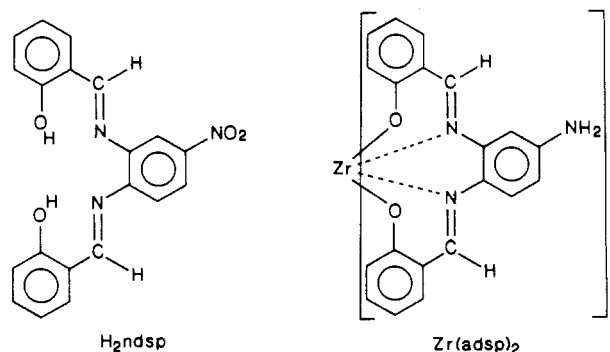
were each confirmed by NMR. The hydrogenation catalyst, 5% or 10% palladium on charcoal (K and K Laboratories), was also used without further purification. The monomer reagent 1,2,4,5-benzenetetra-carboxylic anhydride, PMDA (Aldrich), was recrystallized three times from freshly distilled acetic anhydride that had been dried at reflux over

(1) (a) Rogers, H. G.; Gaudiana, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2669. Rogers, H. G.; Gaudiana, R. A.; Hollinsed, W. C.; Kalyenaraman, P. S.; Manello, J. S.; McGowan, C.; Minns, R. A.; Sahatjian, R. *Macromolecules* **1985**, *18*, 1058. (b) Imai, Y.; Maldar, N. N.; Kakimoto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2077. Ghatge, N. D.; Shinde, B. M.; Mulik, U. P. *J. Macromol. Sci., Chem.* **1985**, *A22*(8), 1109. Babu, G. N.; Samant, S. *Eur. Polym. J.* **1981**, *17*, 421. (c) Evans, J. R.; Orwoll, R. A.; Tang, S. S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 971. Varma, I. K.; Sangita; Choudhary, M. S.; Rao, B. S.; Varma, D. S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1885. Kurita, K.; Murakoshi, H. *Polym. Commun.* **1985**, *26*, 179. Ghosh, M.; Maiti, S. *J. Macromol. Sci., Chem.* **1985**, *A22*(10), 1463. Sen, D.; Bhakta, R. C.; Maiti, S. *Makromol. Chem.* **1985**, *186*, 1625. Maiti, S.; Ray, A. *J. Macromol. Sci., Chem.* **1983**, *A19*(3), 439. Ray, A.; Bhattacharya, V. K.; Roa, Y. V.; Maiti, S. *Eur. Polym. J.* **1983**, *19*, 1195. Emmerling, W. N.; Hallensleben, M. L. *Eur. Polym. J.* **1977**, *13*, 179. (d) Burks, H. D.; St. Clair, T. L. *J. Appl. Polym. Sci.* **1985**, *30*, 2401. (e) Korshak, V. V.; Mognonov, D. M.; Izyneev, A. A.; Dorodhenko, Yu. E. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 595. (f) Archar, B. N.; Fohler, G. M.; Parker, J. A. *J. Polym. Soc., Polym. Chem. Ed.* **1985**, *23*, 801. (g) Bell, V. L.; Kilzer, L.; Hett, E. M.; Stokes, G. M. *J. Appl. Polym. Sci.* **1981**, *26*, 3805. Bell, V. L.; Stump, B. L.; Gager, H. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2275. (h) Varma, I. K.; Geol, R. N.; Varma, D. S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 703. (i) Imai, Y.; Hamaoka, N.; Kakimoto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1291. (j) Varma, I. K.; Rao, B. S. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 545.

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calcium carbide. After it was dried overnight in vacuo, the PMDA melted at 286 °C. The monomer reagent terephthaloyl chloride (Aldrich) was purified by adding an excess amount to hexane, heating at reflux, and then filtering while hot to remove carboxylic acid impurities and undissolved acid chloride. When the solution was cooled, a white precipitate formed in the filtrate, which was suction filtered and dried in vacuo; its melting point was 80 °C.

Solvent purification steps include the reflux and distillation of absolute ethanol from zirconium *n*-butoxide butanol complex (600:40) for subsequent use in the synthesis of $Zr(ndsp)_2$, and the reflux and distillation of *N*,*N*-dimethylformamide (DMF) from P_2O_5 prior to its use in the trial polymerization reactions.

4-Nitro-*N*,*N*'-disalicylidene-1,2-phenylenediamine, H_2ndsp. To a stirred suspension of 15.9 g (0.104 mol) of 4-nitro-1,2-phenylenediamine in 500 mL of absolute ethanol was added 23.0 mL (26.4 g, 0.216 mol) of salicylaldehyde. The mixture was heated and maintained at reflux for ca. 16 h, then cooled, and suction filtered and the product thoroughly washed with absolute ethanol. After air drying, 17.95 g of fluffy yellow Schiff base was obtained; 46% yield.

The purity of the product was confirmed by spotting a dilute methylene chloride solution onto a silica gel TLC plate and eluting with a methylene chloride–ether solution (0.5:25); only one spot was observed in the resultant chromatogram.

Bis(4-nitro-*N*,*N*'-disalicylidene-1,1-phenylenediaminato)zirconium(IV), $Zr(ndsp)_2$. Under a dinitrogen atmosphere (glovebag), a 10.716-g (29.7-mmol) portion of H_2ndsp Schiff base was suspended in 500 mL of dried, freshly distilled absolute ethanol, and 6.4 mL (6.8 g, 14.9 mmol) of zirconium tetra-*n*-butoxide butanol complex and a magnetic stirbar were added. The flask containing the mixture was stoppered, removed from the glovebag, fitted with a condenser to which a drying tube (Drierite-CaH₂) had been attached, and heated at reflux, with stirring, overnight. The mixture was then allowed to cool to room temperature and suction filtered, and the products were thoroughly washed with cold absolute ethanol. After air drying, 8.740 g of yellow, microcrystalline powder was obtained; 97% yield.

The purity was confirmed by TLC with the same chromatography system described above. If needed, $Zr(ndsp)_2$ was recrystallized by using the tetrahydrofuran (THF)–absolute ethanol solvent pair.

Bis(4-amino-*N*,*N*'-disalicylidene-1,2-phenylenediaminato)zirconium-(IV), $Zr(adsp)_2$. In a Parr bottle 8.140 g (10.1 mmol) of pure $Zr(ndsp)_2$ was dissolved in 250 mL of THF (or methylene chloride) and 1.5 g of Pd/C catalyst was added. The mixture was then subjected to a hydrogen gas atmosphere of 55 lb in.⁻² gauge pressure, with agitation, for 24 h or more in a Parr pressure reaction apparatus. Completion of the hydrogenation reaction was confirmed by TLC of the reaction mixture, once again with silica gel plates and a somewhat richer methylene chloride–ether eluting solution (1.0:25); the higher R_f yellow spot of $Zr(ndsp)_2$ was no longer present at the end of the reaction, and a single yellow-orange spot of much lower R_f remained. (It should be noted that hydrogenation beyond this point, up to 3 days, did not cause any additional spots to appear.) When hydrogenation was completed, the catalyst was removed by suction filtration. (*Caution!* Palladium catalyst impregnated with hydrogen is flammable and should not be allowed to become completely dry in air; immersion in water is a suitable precaution.) The filtrate was concentrated by rotary evaporation, and petroleum ether (bp 39–57 °C) was added to induce precipitation. After suction filtration, the light orange microcrystalline powder was washed with cold ethanol, loosely covered, and allowed to air-dry; 6.202 g obtained, 82.2% yield.

The TLC of the product was rechecked by using the same chromatography system used to monitor the hydrogenation, and if needed, $Zr(adsp)_2$ was recrystallized from THF and petroleum ether a second time, by using the above procedure. If a reddish discoloration appeared, additional hydrogenation followed by gravity filtration under a dinitrogen atomsphere was required to remove it.

Trial Polymerization. (A) Polyamic Acid. Recrystallized PMDA, 0.4362 g (2.00 mmol), and $Zr(adsp)_2$, 1.4998 g (2.00 mmol), were separately dissolved in 15 and 20 mL of dried DMF, respectively. They were then mixed together in a three-neck round-bottom flask by addition of small portions of colorless dianhydride solution to the red diamine solution, with stirring, over a period of 1–2 min under a stream of dinitrogen gas. The dianhydride container was rinsed with a few milliliters of fresh, dried DMF, the rinse solution added to the clear red polymerization solutin, and the mixture then heated at 80 °C for 7 h under a positive pressure of dinitrogen gas. After some cooling, the product was isolated by pouring the solution into ca. 400 mL of rapidly stirred anhydrous ether. After several minutes the bright yellow precipitate was suction filtered, then slurried again with anhydrous ether, and refiltered. After drying 1.200 g was obtained; 62.0% yield.

A room-temperature trial following this procedure was also conducted.

(B) Polyamide. Recrystallized terephthaloyl chloride, 0.4060 g (2.00 mmol), and $Zr(adsp)_2$, 1.4998 g (2.00 mmol), were separately dissolved as above, and 1 mL of triethylamine was added to the diamine solution. The colorless diacid chloride solution was then added to the red diamine–triethylamine solution under a dinitrogen stream as described above, with some evolution of gas and a small rise in temperature observed upon mixing. Heating was then initiated, and a temperature of 120 °C was maintained for 20 h under a positive pressure of dinitrogen gas. The product was isolated as above, and 1.236 g of yellow material was obtained; 67.5% yield.

Note that the polymer products will darken significantly if insufficiently washed.

Characterization. All IR spectra were obtained on a Perkin-Elmer 257 grating spectrophotometer as KBr pellets (polystyrene external calibration). ¹H NMR spectra were obtained on a Varian Anaspect EM 360 spectrophotometer in DMSO-d_6 with 1% Me₄Si as the internal standard. UV–vis spectra were obtained on an IBM 9420 spectrophotometer in methylene chloride. Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Viscosities for dilute solutions (0.1 g dL⁻¹) were obtained in *N*-methylpyrrolidone (NMP) at 30.0 °C by using an Ubbelohde suspended level viscometer.

All elemental analyses were performed by Microlytics, the microanalysis laboratory associated with the University of Massachusetts, MA.

X-ray Crystal Structure. Crystals suitable for X-ray structure determination were obtained at 23 °C from the unheated DMF polymerization solutions to which toluene had been added.

In Table I crystal parameter, data collection, and refinement data are collected. No correction for absorption was required (low μ and T_{max}/T_{min} = 1.04). The structure was solved by heavy-atom methods and subsequent difference Fourier syntheses. For each Zr complex molecule, a molecule of DMF and 1.5 molecules of toluene were located in the lattice. The fractional toluene molecule is disordered about an inversion center; only the aromatic ring could be modeled, and then only with a C–C distance constraint of 1.395 Å. No evidence for the methyl group was seen. All non-hydrogen atoms were refined anistropically, and the hydrogen atoms were incorporated as idealized contributions. The NH₂ group of the aniline residue exhibits two-site disorder indicated in Figure 1 as the N(5), N(5') and N(6), N(6') pairs. The occupancies were refined with a unit occupancy constraint, yielding sof(N(5)) = 0.68 (1) and sof(N(6)) = 0.65 (1). All software is contained in the SHELXTL program library (Nicolet Corp., Madison, WI).

Atomic coordinates are given in Table II. Additional crystallographic data are available as supplementary material.

Results

Synthesis. The eight-coordinate dinitro Schiff-base complex $Zr(ndsp)_2$ was prepared from $Zr(O\text{-}n\text{-}Bu)_4$·*n*-BuOH and the premade Schiff-base ligand H_2ndsp and then catalytically hy-
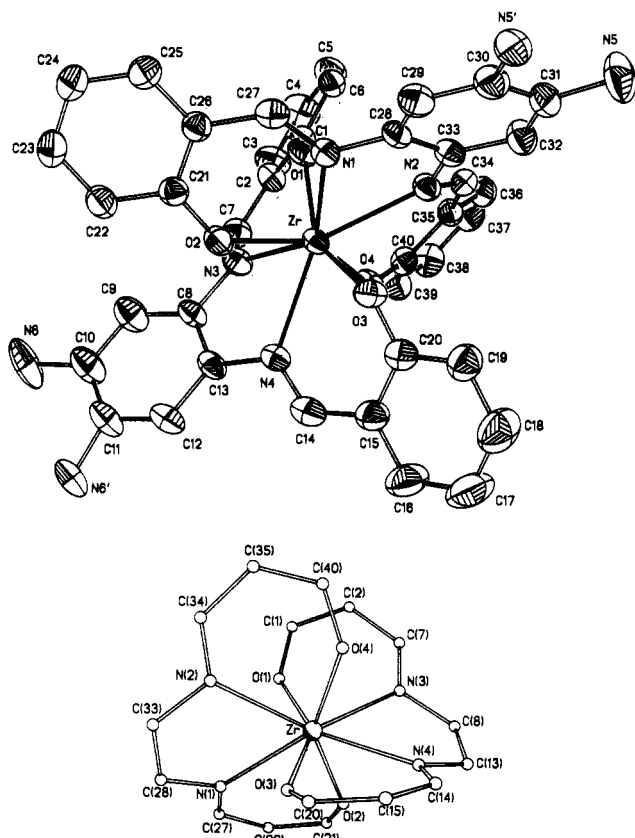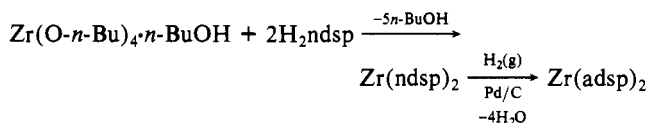
Figure 1. (a) Top: ORTEP plot showing the Zr(adsp)₂ atom-numbering scheme and molecular structure. Thermal ellipsoids are at the 40% probability level. (b) Bottom: A different view showing just the Zr coordination sphere.

drogenated to produce the diamino complex Zr(adsp)₂ according to the reaction scheme

$$Zr(O\text{-}n\text{-}Bu)_4\cdot n\text{-}BuOH + 2H_2ndsp \xrightarrow{-5n\text{-}BuOH}$$

$$Zr(ndsp)_2 \xrightarrow[-4H_2O]{\frac{H_2(g)}{Pd/C}} Zr(adsp)_2$$

Characterization. The physical and spectral data, i.e., the percent yield, color, melting behavior, elemental analysis (for the new compounds only), and IR, NMR, and UV–vis spectral data are collected in Table III for Zr(adsp)₂, Zr(ndsp)₂, and the corresponding free nitro Schiff-base ligand, H₂ndsp.

The X-ray structure results, summarized in Table IV–VII (Tables V and VII are supplementary material), are consistent with a dodecahedral (pseudo D_{2d} or $\overline{4}2m$) coordination polyhedron, with $\theta_A = 33.6°$, $\theta_B = 72.6°$, and Zr–N(av)/Zr–O(av) = 2.419 Å/2.085 Å = 1.16.[2] The intersecting donor atom trapezoids in Zr(adsp)₂ are essentially perpendicular and very close to planar (with or without Zr) despite the extensive puckering of both ligand backbones. The regularity of the dodecahedron coordination sphere is further indicated by the consistency of the δ angles (22.5, 22.6, 24.8, and 23.6°), which are the angles between the normals to the triangular faces that are situated on each side of the four b edges.[4] Therefore, as was the case for the unsubstituted Zr(dsp)₂ complex, all parameters point to a dodecahedral geometry with each quadridentate ligand spanning *mam* edges[2] and with oxygen and nitrogen atoms arranged in accordance with theoretical predictions.[5] Outside of the coordination sphere, the X-ray

(2) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963,** 2, 235.
(3) Archer, R. D.; Day, R. O.; Illingsworth, M. L. *Inorg. Chem.* **1979,** 18, 2908.
(4) Drew, M. G. B. *Coord. Chem. Rev.* **1977,** 24, 179. Although the φ angles for Zr(adsp)₂ were not determined, they would be very small due to the proximity to planarity of each donor atom trapezoid and thus would be much closer to the ideal dodecahedral value (0°) than the ideal square antiprism value (24.5°) or the ideal bicapped trigonal prism value (14.1°).
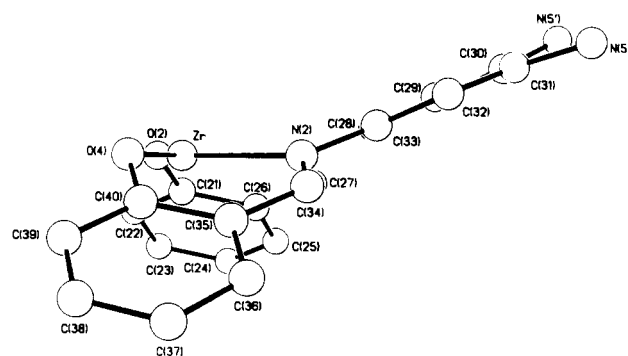
Figure 2. Side-on view of one of the adsp²⁻ ligands coordinated to zirconium, showing the planarity of the O,N,N′,O′ donor atom set and the puckering of the ligand backbone.

structure data show that the predominant source of the adsp²⁻ ligands' nonplanarity is rotation about the nitrogen–phenyl bond, the average torsion angle being 25.9° (see Table VII). Also note that there is only one amino group on each of the adsp²⁻ ligands; the unprimed and primed labels N(5), N(5′)) (or N(6), N(6′)) in Figures 1 and 2 indicate that the amine group may be found in either of these two locations in an approximately 2:1 ratio (see Experimental Section).

Trial Polymerizations. Trial polymerizations were conducted by combining DMF solutions of dianhydride or diacid chloride with solutions of Zr(adsp)₂ at various reaction times and temperatures. The yellow products that gave the highest viscosity solutions were obtained from reactions conducted at 80 °C for 7 h and 120 °C for 16 h, respectively, by using anhydrous ether to precipitate and *thoroughly* wash the product. Insufficient washing results in fairly rapid darkening at the compound's surface upon air filtration and/or standing in air. Probably due to the extensive handling, yields were not quantitative.

Polymer Characterization. The infrared spectrum of the product of the PMDA reaction showed carbonyl stretching frequencies at ∼1700 and 1650 cm⁻¹, consistent with the presence of carboxylic acid and amide groups, and did not show any absorbance near 1775 cm⁻¹, the CO stretching frequency of unreacted PMDA. Likewise for the diacid chloride reaction, the absorbance at 1660 cm⁻¹ indicates that amide groups are present, and the lack of a ∼1750-cm⁻¹ absorbance indicates that free acid chloride groups are absent. (Please note that while the polymerization solvent, DMF, would also be expected to have an amide absorbance, it could not account for the *observed* amide bands because the other absorbance that DMF would be expected to show are either weak or absent.) Both products' infrared spectra did show absorbances at approximately 1600 cm⁻¹ (C=N) and 1320 cm⁻¹ (coordinated O–phenyl) identical with those of Zr(adsp)₂.

Dilute-solution inherent viscosities, [η]ᵢₙₕ, of 0.19 dL g⁻¹ for both polymerization products compare favorably with that of Zr(adsp)₂, 0.02 dL g⁻¹, and match those of previously published coordination polymers of this type.[6] Preliminary GPC results,[7] in addition to the IR and viscosity data, further support the contention that polymerization of Zr(adsp)₂ did actually occur.

An observed polymerization product melting/decomposition point of >300 °C indicates that the high-temperature stability of the zirconium complex is largely retained in these oligomers. Suitable solvents include dimethyl sulfoxide (DMSO) and strong acids, as well as the reaction solvent, DMF, and the viscosity solvent NMP.

Discussion

Synthesis of Zr(adsp)₂. Of the two envisionable routes to Zr(adsp)₂ from the ligand H₂ndsp, (1) hydrogenate the nitro group to form H₂adsp and then coordinate it to zirconium or (2) co-

(5) Clark, R. J. H.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1962,** 2460.
(6) Archer, R. D.; Illingsworth, M. L.; Rau, D. N.; Hardiman, C. J. *Macromolecules* **1985,** 18, 1371.
(7) Archer, R. D., private communication, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U^a		x	y	z	U^a
Zr	135 (1)	2069 (1)	2509 (1)	40 (1)*	C(20)	2246 (4)	2872 (4)	1646 (4)	52 (2)*
O(1)	-839 (3)	2037 (3)	3531 (2)	52 (1)*	C(21)	-131 (4)	-171 (4)	2734 (3)	46 (2)*
O(2)	6 (3)	564 (2)	2240 (2)	50 (1)*	C(22)	-846 (5)	-1047 (4)	2291 (4)	61 (2)*
O(3)	1775 (3)	2438 (3)	2261 (2)	53 (1)*	C(23)	-1010 (6)	-1831 (4)	2808 (4)	72 (3)*
O(4)	-421 (3)	3296 (3)	1965 (2)	56 (1)*	C(24)	-442 (6)	-1775 (4)	3765 (4)	70 (3)*
O(5)	2831 (5)	5841 (4)	3228 (4)	113 (3)*	C(25)	301 (5)	-926 (4)	4198 (4)	60 (2)*
N(1)	1389 (3)	1589 (3)	3868 (3)	43 (1)*	C(26)	450 (4)	-113 (4)	3699 (4)	47 (2)*
N(2)	1109 (3)	3436 (3)	3698 (3)	45 (2)*	C(27)	1251 (4)	753 (4)	4179 (4)	48 (2)*
N(3)	-1867 (3)	1494 (3)	1664 (3)	49 (2)*	C(28)	2298 (4)	2334 (4)	4417 (3)	44 (2)*
N(4)	-126 (4)	1745 (3)	798 (3)	45 (2)*	C(29)	3322 (4)	2148 (4)	4985 (4)	56 (2)*
N(5)	4824 (7)	4602 (6)	6033 (6)	94 (4)*	C(30)	4181 (5)	2893 (4)	5510 (4)	60 (2)*
N(5')	5179 (11)	2672 (11)	6031 (10)	62 (6)*	C(31)	4026 (5)	3853 (4)	5462 (4)	63 (2)*
N(6)	-3969 (7)	-1222 (7)	-751 (7)	104 (4)*	C(32)	3025 (5)	4047 (4)	4850 (4)	59 (2)*
N(6')	-2471 (13)	-618 (11)	-1860 (10)	74 (6)*	C(33)	2159 (4)	3287 (4)	4339 (3)	46 (2)*
N(7)	1543 (5)	6139 (4)	1919 (4)	88 (3)*	C(34)	738 (4)	4236 (4)	3832 (4)	49 (2)*
C(1)	-1820 (4)	2329 (4)	3596 (3)	46 (2)*	C(35)	-271 (4)	4516 (4)	3238 (4)	48 (2)*
C(2)	-2787 (4)	2201 (4)	2816 (4)	50 (2)*	C(36)	-726 (5)	5287 (4)	3587 (4)	59 (2)*
C(3)	-3797 (5)	2519 (5)	2922 (4)	71 (3)*	C(37)	-1718 (5)	5565 (4)	3063 (4)	65 (3)*
C(4)	-3867 (6)	2953 (5)	3770 (5)	80 (3)*	C(38)	-2217 (5)	5099 (4)	2173 (4)	68 (3)*
C(5)	-2923 (6)	3066 (5)	4537 (4)	70 (3)*	C(39)	-1781 (5)	4355 (4)	1794 (4)	63 (2)*
C(6)	-1924 (5)	2757 (4)	4470 (4)	53 (2)*	C(40)	-818 (4)	4030 (4)	2322 (4)	49 (2)*
C(7)	-2761 (4)	1708 (4)	1913 (4)	55 (2)*	C(41)	5425 (10)	8243 (10)	1946 (9)	182 (7)*
C(8)	-2030 (4)	901 (4)	786 (4)	52 (2)*	C(42)	4537 (11)	8355 (11)	1276 (11)	233 (10)*
C(9)	-2987 (5)	165 (5)	420 (4)	75 (3)*	C(43)	3829 (14)	7492 (15)	663 (13)	254 (12)*
C(10)	-3088 (6)	-419 (5)	-426 (5)	85 (3)*	C(44)	4103 (14)	6716 (15)	859 (11)	229 (11)*
C(11)	-2214 (5)	-234 (5)	-906 (4)	81 (3)*	C(45)	4972 (17)	6551 (14)	1542 (13)	186 (10)*
C(12)	-1228 (5)	474 (4)	-526 (4)	64 (2)*	C(46)	5649 (13)	7336 (15)	2100 (11)	171 (9)*
C(13)	-1130 (4)	1055 (4)	325 (3)	50 (2)*	C(47)	6201 (14)	9183 (11)	2629 (10)	257 (12)*
C(14)	536 (5)	2150 (4)	308 (4)	56 (2)*	C(48)	2185 (6)	5610 (6)	2433 (5)	93 (3)*
C(15)	1664 (5)	2768 (4)	666 (4)	60 (2)*	C(49)	814 (9)	5779 (9)	1004 (7)	167 (6)*
C(16)	2230 (6)	3232 (6)	39 (5)	89 (3)*	C(50)	1545 (13)	7092 (9)	2324 (8)	214 (9)*
C(17)	3334 (7)	3777 (7)	328 (6)	112 (4)*	C(51)	4394 (9)	57 (12)	3936 (11)	295 (9)
C(18)	3906 (6)	3841 (6)	1282 (6)	100 (4)*	C(52)	5431 (10)	457 (9)	4601 (4)	178 (5)
C(19)	3371 (5)	3408 (5)	1932 (5)	68 (3)*	C(53)	6166 (10)	554 (10)	5513 (4)	188 (5)

^{a} Asterisks denote equivalent isotropic U values, defined as one-third of the trace of the orthogonalized U_{ij} tensor.

ordinate the H$_2$ndsp and then hydrogenate, the latter proved to be more viable due to the considerable reactivity of H$_2$adsp. Thus, the coordination of H$_2$ndsp to zirconium (2:1 stoichiometry) was conducted in a manner analogous to the coordination of the ester-substituted Schiff base ethyl *N,N'*-disalicylidene-3,4-diaminobenzoate to zirconium,[8] which is a reaction promoted by the chelate effect. The catalytic hydrogenation of the two nitro groups to amino groups ensued, *without* hydrogenation of the Schiff-base imine bonds (see below) to produce the Zr(adsp)$_2$ product.

Spectra. In addition to having O—H, C=N, and phenyl—O IR absorbances that are analogous to those for H$_2$dsp, H$_2$ndsp displays bands at 1512 and 1339 cm^{-1} that are typical of nitro groups. Upon coordination to form Zr(ndsp)$_2$, the nitro group and C=N frequencies undergo minor changes whereas the phenyl—O frequency is characteristically shifted[3] from approximately 1280 to 1320 cm^{-1}, and the O—H band is no longer present (once the ethanol is completely removed). The absence of the nitro group bands, the presence of a N-H absorbance, and the persistence of the C=N band in the IR spectrum of Zr(adsp)$_2$ are consistent with the hydrogenation of the nitro groups to amine groups, without the hydrogenation of the coordinated imine groups.

The ^{1}H NMR spectrum of H$_2$ndsp shows a complicated aromatic proton multiplet (δ 7.8–6.5), and an imino proton singlet (δ 8.3) downfield from the usual aromatic proton region, as does H$_2$dsp (δ 7.4–6.9 and 8.5); however, the electron-withdrawing nitro group further deshields nearby aromatic protons in the diamine ring, resulting in distinctive aromatic proton chemical shifts of δ 9.0 and 8.1. The coordination of this compound is affirmed by the almost 1 ppm upfield change in chemical shift for certain aromatic protons in its aldehyde ring, identical with the observed for the coordination of H$_2$dsp.[3] And finally, hydrogenation of the nitro groups of Zr(ndsp)$_2$, without hydrogenation of the imine bonds, is affirmed by the absence of the nitro-deshielded aromatic protons at δ 9.0 and 8.1, the retention of the upfield-shifted protons associated with ligand coordination, the appearance of a somewhat broad singlet at δ 5.45 that exchanges with D$_2$O (the amine protons' chemical shift), and the retention of an imino proton signal at δ 8.5. This imino proton signal is clearly a doublet with a very small coupling constant in the Zr(adsp)$_2$ spectrum, in contrast to the singlet imino proton signal observed for H$_2$ndsp. This difference is most likely explained by the freedom of motion present in H$_2$ndsp, which averages the chemically inequivalent imine protons and which is largely lost upon coordination. We suspect that the imine signal in the Zr(ndsp)$_2$ NMR spectrum is also very finely split into a doublet, but this region is unfortunately obscured by the nitro-deshielded aromatic proton signals, which are ring-coupled multiplets.

General support for the proposed formulations can also be obtained from the ultraviolet–visible spectra in that the number of major bands is the same for substituted and unsubstituted complexes (3) and in that the extinction coefficients are of the same order of magnitude as well.[3] It is interesting to note that the peak having the second highest extinction coefficient in the Zr(adsp)$_2$ complex, 376 nm, falls very close to the K band in *p*-nitroaniline, 381 nm, in which the *electron-withdrawing* nitro group is in conjugation with the amino group (see below), and the peak having the second highest extinction coefficient in the Zr(ndsp)$_2$ complex, 308 nm, falls in between the K bands of *p*-nitrotoluene (274 nm) and *p*-nitrophenol (318 nm).

Structure of Zr(adsp)$_2$. Comparison of the Zr(adsp)$_2$ average Zr–N and Zr–O bond lengths to those of Zr(dsp)$_2$[3] reveals that both are only marginally shorter (0.009 and 0.012 Å, respectively) in the diamine complex. *If* these differences are significant, a convenient explanation as to why this occurs is that the amino groups of Zr(adsp)$_2$ are able to release additional electron density

(8) Illingsworth, M. L.; Archer, R. D. *Polyhedron* **1982**, *1*, 487. The ester-substituted quadridentate Schiff-base ligand can alternately be named 4-(carboxyethyl)-*N,N'*-disalicyclidene-1,2-phenylenediamine, H$_2$cedsp. Thus, the complex reported is better named bis(4-(carboxyethyl)-*N,N'*-disalicylidene-1,2-phenylenediaminato)zirconium(IV), Zr(cedsp)$_2$.

Table III. Characterization Data for the Nitro Schiff-Base Ligand and New Zirconium Complexes

Physical Data

	H$_2$ndsp	Zr(ndsp)$_2$	Zr(adsp)$_2$
yield, %	>40	>90	>80
color	yellow	yellow	light orange
mp, °C	212–213	>300	>300^a
elemental anal.^{b}		C, 59.32 (59.33)^c	C, 64.06 (63.97, 63.74)^d
		H, 3.24 (3.42)	H, 4.03 (4.09, 4.11)
		N, 10.38 (10.34)	N, 11.21 (11.04, 11.10)
		Zr, 11.26 (11.1)	Zr, 12.26 (12.1, 12.2)

Spectral Data

assignt	H$_2$ndsp	Zr(ndsp)$_2$	Zr(adsp)$_2$
		Infrared Data (cm^{-1})^e	
O—H	3300–3600		
N—H			3300–3410 mw
C=N	1612 s	1610 s	1612 s
N—O	1512 m	1512 m	
	1339 m	1341 m	
Ph—O	1275 m	1320 m	1318 m
		^{1}H NMR (δ)^f	
H—O	11.9 s (2)		
H—C=N	8.3 s (2)	8.45 (2)	8.5 d (2)^g
arom H	9.0 d (2),^{h}	8.85 d (2),^{h}	h
	8.1 (1)^h	8.15 (1)^h	
	7.8–7.2 m (4),	7.9–6.4 m (6)	7.4–6.1 m (6)
	7.1–6.5 (4)		
		5.9–5.6 d (2)^i	5.8–5.6 (2)^i
H—N amine			5.45 s (2)^j
		Ultraviolet–Visible Data (cm^{-1})^k	
		22 400 sh	ill-def sh
	28 800 (4.35)	25 400 (4.47)	26 600 (4.57)
		ill-def sh	
	34 300 (4.35)	32 400 (4.62)	32 900 (4.43)
	43 700 (4.39)	39 900 (4.81)	41 300 (4.82)

^{a} Some discoloration is seen prior to 300 °C. ^{b} Elemental analyses were performed by Microlytics, P.O. Box 199, South Deerfield, MA 01373. ^{c} Calculations are based on the formula C$_{40}$H$_{26}$N$_6$O$_8$Zr; experimentally determined values are in parentheses. ^{d} Calculations are based on the formula C$_{40}$H$_{30}$N$_6$O$_4$Zr; experimentally determined values are for one recrystallization and three recrystallizations. ^{e} Conditions: KBr pellets; polystyrene as external calibration. Abbreviations: s = strong, m = medium, w = weak. ^{f} In DMSO-d_6 with 1% Me$_4$Si as internal standard. The relative peak integration values are given in parentheses. Abbreviations: s = singlet, d = doublet, m = multiplet. ^{g} Indicates that the imine bonds are not hydrogenated; the observed coupling constant is very small. ^{h} Aromatic protons downfield shifted due to the nitro group. ^{i} Aromatic protons shifted upfield due to coordination to zirconium. ^{j} Protons are exchangable with D$_2$O. ^{k} In CH$_2$Cl$_2$ solutions. Logarithms of the extinction coefficients are in parentheses. Abbreviations: sh = shoulder, ill-def = ill-defined.

into the coordination sphere, thus easing the interatomic repulsions and allowing the donor atoms to approach the zirconium atom more closely. But while this is a tempting explanation of these facts, it is not convincing unless other evidence can be found. Fortunately, then, further comparisons reveal the following: (1) the distortion of the ligand trapezoids from planarity is slightly less for Zr(adsp)$_2$; (2) the interpenetrating trapezoids are more nearly perpendicular for Zr(adsp)$_2$ (90.0 and 89.8° between pairs of trapezoidal planes vs 89.2 and 89.2° for Zr(dsp)$_2$; for deviations in angstroms from mean trapezoidal planes, see Table V, included with the supplementary material); (3) the dodecahedral coordination sphere is significantly more regular for Zr(adsp)$_2$ on the basis of the δ angles (22.5, 22.6, 24.8, and 23.6° vs 28.0, 19.6, 22.5, and 25.8° for Zr(dsp)$_2$). Further significant evidence is that the *reactivity* of these amino groups is less than that of their completely organic counterparts (see below). And even the proximity of the allowed long-wavelength electronic transitions of Zr(adsp)$_2$ and *p*-nitroaniline, mentioned above, is consistent with an electron-withdrawing nature for the coordination sphere.

Another comparison with Zr(dsp)$_2$ can be made on the basis of the three parameters that describe the shape of these dode-

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for the Coordination Sphere of Zr(adsp)$_2$^{a}

Distances			
Zr–O(1)	2.088 (4)	Zr–O(3)	2.075 (4)
Zr–O(2)	2.092 (3)	Zr–O4	2.086 (4)
Zr–N(1)	2.401 (4)	Zr–N(3)	2.412 (4)
Zr–N(2)	2.430 (4)	Zr–N(4)	2.431 (4)
Bond 1^b			
O(1)–C(1)	1.327 (7)	O(3)–C(20)	1.299 (7)
O(2)–C(21)	1.307 (6)	C(4)–C(40)	1.322 (7)
Bond 2			
C(1)–C(2)	1.402 (6)	C(20)–C(15)	1.420 (7)
C(21)–C(26)	1.405 (7)	C(40)–C(35)	1.410 (7)
Bond 3			
C(2)–C(7)	1.446 (8)	C(15)–C(14)	1.447 (7)
C(26)–C(27)	1.443 (6)	C(35)–C(34)	1.455 (7)
Bond 4			
C(7)–N(3)	1.279 (8)	C(14)–N(4)	1.278 (8)
C(27)–N(1)	1.289 (7)	C(34)–N(2)	1.289 (7)
Bond 5			
N(3)–C(8)	1.426 (6)	N(4)–C(13)	1.419 (6)
N(1)–C(28)	1.427 (5)	N(2)–C(33)	1.439 (6)
Bond 6			
C(8)–C(13)	1.394 (8)	C(28)–C(33)	1.383 (8)
Angles			
O(1)–Zr–O(2)	96.7 (1)	O(1)–Zr–N(2)	74.7 (1)
O(1)–Zr–O(3)	145.6 (1)^c	O(1)–Zr–N(3)	73.5 (1)
O(1)–Zr–O(4)	94.3 (2)	O(1)–Zr–N(4)	140.3 (1)
O(1)–Zr–N(1)	76.4 (1)		
O(2)–Zr–O(3)	96.3 (1)	O(2)–Zr–N(2)	141.5 (1)
O(2)–Zr–O(4)	144.6 (1)^c	O(2)–Zr–N(3)	75.4 (1)
O(2)–Zr–N(1)	74.0 (1)	O(2)–Zr–N(4)	74.6 (1)
O(3)–Zr–O(4)	93.2 (1)	O(3)–Zr–N(3)	140.8 (1)
O(3)–Zr–N(1)	76.8 (1)	O(3)–Zr–N(4)	74.0 (1)
O(3)–Zr–N(2)	75.3 (1)		
O(4)–Zr–N(1)	141.4 (1)	O(4)–Zr–N(3)	75.7 (1)
O(4)–Zr–N(2)	73.9 (1)	O(4)–Zr–N(4)	75.5 (1)
N(1)–Zr–N(2)	67.5 (1)^c	N(1)–Zr–N(4)	133.9 (2)
N(1)–Zr–N(3)	133.6 (1)		
N(2)–Zr–N(3)	133.6 (2)	N(2)–Zr–N(4)	134.7 (1)
N(3)–Zr–N(4)	149.9 (1)^c		

^{a} Estimated standard deviations are indicated in parentheses; atoms are labeled to agree with Figure 1. ^{b} These numbers refer to the bonds indicated:
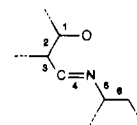
^{c} Used to calculate θ_A = 33.6° (33.4°) and θ_B = 72.6° (73.0°).^{2} The values in parentheses are θ_A and θ_B values for Zr(dsp)$_2$.^{3} The hard-sphere model predicts 36.9 and 69.5°, and the most favorable model predicts 35.2 and 73.5°, respectively.^{2}

cahedra, θ_B, and Zr–N(av)/Zr–O(av).^{2} While these parameters are actually independent of the metal to donor atom bond lengths (as long as the ratio is preserved), the significantly increased δ-angle regularity of the Zr(adsp)$_2$ dodecahedral coordination sphere does require a change in its θ angles. The changes of +0.2 and −0.4° from the θ_A and θ_B values of Zr(dsp)$_2$, however, are also of only marginal significance; also see Table IV for a comparison of values from the hard-sphere model and the most favorable model. The Zr–N(av)/Zr–O(av) ratio is only different by 0.01 (1.16 for Zr(adsp)$_2$ vs 1.15 for Zr(dsp)$_2$), so *if* the amino groups are causing a decrease in the size of the coordination dodecahedra, they are causing quite a uniform decrease and a slightly more regular shape as well. (The "more regular shape" is evidently achieved for the most part by a contraction of the *g* dodecahedral edges of Zr(adsp)$_2$ by approximately 0.03 Å; see Table VI.)

Table VI. Dodecahedral Edges in the $Zr(adsp)_2$ Coordination Sphere

edge[a]	edge length, Å	edge	edge length, Å
		a Edges[b]	
N(1)–N(2)	2.69	N(3)–N(4)	2.67
		mean	2.68 (2.67)[c]
		b Edges[b]	
O(1)–O(2)	3.13	O(3)–O(4)	3.02
O(1)–O(4)	3.06	mean	3.07 (3.09)[c]
O(2)–O(3)	3.10		
		g Edges[b]	
O(1)–N(1)	2.79	O(3)–N(2)	2.77
O(1)–N(2)	2.76	O(4)–N(3)	2.77
O(2)–N(3)	2.77	O(4)–N(4)	2.78
O(2)–N(4)	2.75	mean	2.77 (2.80)[c]
O(3)–N(1)	2.79		
		m Edges[b]	
O(1)–N(3)	2.71	O(3)–N(4)	2.73
O(2)–N(1)	2.72	mean	2.72 (2.72)[c]

Edge Length Ratios

b/a	1.15 (1.16)[c]	*b/g*	1.11 (1.10)[c]
b/m	1.13 (1.13)[c]		

[a] Atoms are labeled as shown in Figure 1. [b] Standard Hoard and Silverton symbolism.[2] [c] Corresponding values for the unsubstituted complex $Zr(dsp)_2$[3] are given in parentheses.

Outside of the coordination sphere, there are several structural features that are also noteworthy. One, which is evident from Figure 2 and from the torsion angles (given in Table VII of the supplementary material), is that most of the ligand puckering in $Zr(adsp)_2$ is due to rotation about the phenyl–N bonds, as is the case for $Zr(dsp)_2$. The distortion of these conjugated ligands from planarity is necessary because the ligand must expand its O to O' distance to accommodate the large zirconium atom. Another feature is that the average imine bond length is even slightly shorter for $Zr(adsp)_2$ than for $Zr(dsp)_2$, 1.28 vs 1.30 Å, indicating that this is a very localized double bond. From the crystal-packing diagram, it is apparent that there is no stacking of planar phenyl rings between the $Zr(adsp)_2$ molecules or between $Zr(adsp)_2$ and toluene molecules.

One last difference between the substituted and unsubstituted zirconium complexes is that, even if the ligands were planar, addition of the nitro or amino substituent groups would remove the planes of symmetry that lie perpendicular to the plane of each ligand, rendering these complexes "S_n-less", i.e. C_2 rather than C_{2v}. Therefore, the substituted complexes should potentially be resolvable into optically active isomers.

Trial Polymerization. The problems of excessively high T_g, low solubility, and difficulty of cyclization (for polyimides) are all being addressed by this approach. This becomes apparent when the structure of $Zr(adsp)_2$ is related to the kind of structural modifications that have already been shown to be beneficial for wholly aromatic polyamides and polyimides: (1) $Zr(adsp)_2$ possesses noncoplanar phenyl moieties, as do biphenylene-based diamines,[1a] which are known to diminish crystallinity and interchain attractions. (2) The two amino groups of $Zr(adsp)_2$ are not collinear with the axis that bisects the ligands; rather, they are oriented more like the *m,m*-biphenylenediamines, which gave the lowest T_g's of the ring-substituted isomers studied.[1g] (3) The coordinated zirconium structural unit constitutes a heteroatomic group, which, like other heteroatoms and heteroatomic groups, causes the rigid aromatic moieties in the polymer to farther apart, i.e. more "dilute".[1d,f] Copolymerization has also widely been used for this purpose.[1b–h]

In addition to these three "resemblances", ligand motion via nonrigidity (which is characteristic of eight-coordinate complexes) and/or via inversion of the ligand puckering[8] may be a source of additional flexibility. (As was already pointed out, less structural rigidity may permit more complete cyclization.[1e])

Concerning the polymerization reaction conditions for $Zr(adsp)_2$, we have found that the temperature employed for po-

lymerization of analogous organic diamines is too low. For example, 0 °C or room temperature is typically sufficient to obtain a high degree of polymerization between an aromatic organic diamine and a dianhydride to form a polyamic acid;[1b,d,f–h,9] however, our room-temperature polymerization product had a significantly lower viscosity than our 80 °C polymerization product. therefore, we conclude that the amino groups of $Zr(adsp)_2$ are less reactive than their organic counterparts. Please note that this lower amino group reactivity, if borne out, could be readily accounted for by the greater delocalization of the amino group electrons caused by the zirconium coordination sphere, as proposed earlier in this paper. This method of preparing coordination polymers, "ligand-centered polymerization" (LCP), was attempted once before for a diester-substituted zirconium complex,[8] but the temperatures required for polymerization in that case (>250 °C) proved to be excessive. Also note, however, that while examples of the use of the LCP approach are not abundant, the method continues to receive attention,[10] especially with olefinic substituents.[10c]

The infrared spectral results cited in the previous section are consistent with those observed for organic polyamic acids and polyamides and consistent with the preservation of the eight-coordinate structural unit.

The inherent viscosities of dilute "polymer" solutions and the preliminary GPC results[7] indicate that these polymers are already comparable to some previously published coordination polymers.[6,10b,11]

Simple melting/decomposition behavior of our polymer samples and some preliminary solubility tests have been encouraging, vis à vis the improvements that we are trying to make, but it is not likely that we are dealing with very much more than oligomers thus far. The greatest potential that we can see for $Zr(adsp)_2$ is in copolymerizations with other diamines that are known to give high polymers. In this way, the relative amount of $Zr(adsp)_2$ can be adjusted to tailor polymeric products for specific uses.

Conclusions

The three primary conclusions that we have arrived at in this paper are that (1) $Zr(adsp)_2$, and eight-coordinate complex having two free amino groups, has been successfully prepared in high yield, (2) the delocalization of the amino group electrons is probably increased by the coordinated zirconium, thus accounting for the lower reactivity of the amino groups and (perhaps) a marginally smaller size of the coordination dodecahedron compared to that of $Zr(dsp)_2$, and (3) $Zr(adsp)_2$ has been shown to participate in polymerization reactions under fairly mild conditions without decomposition of the eight-coordinate structural unit.

(9) Imai, Y.; Kojima, K. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 2091.
(10) (a) Spiratos, M.; Airimei, A.; Voiculescu, N. *Angew. Makromol. Chem.* **1986**, *138*, 159. (b) Kothandaraman, H.; Venkatarao, K.; Raghavan, A.; Chandrasekaran, V. *Polym. Bull. (Berlin)* **1985**, *13*, 353. Simon, R. A.; Mallonk, T. E.; Daube, K. A.; Wrighton, W. S. *Inorg. Chem.* **1985**, *24*, 3119. (c) Calvert, J. M.; Peebles, D. L.; Nowak, R. J. *Inorg. Chem.* **1985**, *24*, 3111. Kanda, S.; Murray, R. W. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3010. Calvert, J. M.; Schmehl, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1983**, *22*, 2151. Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 1283.
(11) Many coordination polymers contain rigid structures that are easily packed together and thus are too insoluble for viscosity determination; cf. ref 10a and: Deshpande, U. G.; Shah, J. R. *J. Macromol. Sci., Chem.* **1986**, *A23*(1), 97. Vicente, R.; Ribas, J.; Cassoux, P.; Valade, L. *Synth. Met.* **1986**, *13*, 265.

(copolymer), 111291-35-1; 4-nitro-1,2-phenylenediamine, 99-56-9; salicylaldehyde, 90-02-8; terephthaloyl chloride, 100-20-9.

Supplementary Material Available: Tables of deviations (in angstroms) from the least-squares mean trapezoidal planes of the Zr(adsp)₂ coordination sphere and dihedral angles (Table V), torsion angles in the adsp²⁻ ligands (Table VII), bond distances, bond angles, anisotropic temperature coefficients, and hydrogen atom coordinates (8 pages); a listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Resolution and Circular Dichroism of the Optical Isomers of Tris(2,4-pentanedionato)ruthenium(III)

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The enantiomeric isomers of [Ru^{III}(acac)$_3$] (acac = 2,4-pentanedionate) were completely resolved by HPLC on a column of porous silica gel coated with cellulose tris(phenylcarbamate). The configurations Δ and Λ are assigned to the isomers in the first and second fractions eluted by hexane/propanol, respectively. The assignment of the absolute configuration was based on the theoretically predicted circular dichroism in the intense ligand-exciton band at around 36 × 10³ cm⁻¹. Three absorption bands of [Ru(acac)$_3$] observed in the range of (18–40) × 10³ cm⁻¹ are ascribed to the excited states, which are the configuration-interaction admixtures of the ligand-to-metal charge-transfer (LMCT) excited states and the ligand (π,π^*) excited triplets and singlets. The LMCT excited states also interact with the ground-state configurations and split the ground-state sublevels. Theory predicts that circular dichroism in the ligand (π,π^*) excitations from the lowest ground-state sublevel is reversed in this particular open-shell complex with reference to those in the ligand (π,π^*) exciton bands found for the corresponding isomers with no low-lying charge-transfer for excited states.

Introduction

[Ru^{III}(acac)$_3$] (acac = 2,4-pentanedionate) has no ionic charge, and thus resolution of the enantiomeric isomers can not be effected by fractional precipitation with an oppositely charged resolving reagent. So far, a good number of papers have been devoted to resolutions of the optical isomers of noncharged complexes by liquid chromatography on chiral sorbent columns.[1-7] However only partial resolution has been obtained. In the present work, we achieved a complete resolution of the enantiomers of [Ru(acac)$_3$] by high-performance liquid chromatography (HPLC) on a column of porous silica gel coated with cellulose tris(phenylcarbamate). The isomers in the first and the second fractions of elution are of configurations Δ and Λ, respectively. The present assignment is based on the theoretically predicted circular dichroism (CD) in the intense absorption band at around 36 × 10³ cm⁻¹, which is predominantly characterized as the ligand (π,π^*) exciton band. The assignment, however, is also supported by the CD spectrum of partly resolved [Ru(acac)$_3$] if the asymmetric synthesis yields the Δ isomer in excess.[8] The CD sign was reproduced with the enantiomer separated by the alternative method.[9]

Chromatographic resolution of the optical isomers of [Co^{III}(acac)$_3$], [Cr^{III}(acac)$_3$] and [Al^{III}(acac)$_3$] was carried out[10] on a column of silica gel coated with (+)-poly(triphenylmethyl methacrylate).[11] The Δ isomer was in the earlier eluted fraction. In the present work, we also applied this column. However, the column showed no chiral recognition ability for [Ru(acac)$_3$].

[Ru(acac)$_3$] exhibits three absorption bands in the visible and ultraviolet region. These bands are attributable to the lowest excited states, which are the configuration-interaction admixtures of the ligand-to-metal charge-transfer (LMCT) excited states and the ligand (π,π^*) excited triplets and singlets with varied predominant characters. The LMCT excited states also interact with the ground-state configurations and, as a result, split the ground-state sublevels. In this particular open-shell complex, the CD sign in the ligand (π,π^*) excitation from the lowest component state of the split ground-state sublevels is reversed with reference to that of the corresponding exciton band of the complexes with

no low-lying charge-transfer excited states. The closed-shell tris(β-diketonato) complexes of Δ configuration shows a negative and a positive CD band with increasing wavenumber in the ligand (π,π^*) band.[12] It was suggested that simple exciton model yields uncertainties in analysis of the CD spectra of open-shell complexes.[13] In this paper, we present a model which can reasonably describe the lowest excited states of [Ru(acac)$_3$] and correctly reproduce the circular dichroism reversed with reference to that of the corresponding exciton band of the complexes with no low-lying charge-transfer excited states.

Experimental Section

[Ru^{III}(acac)$_3$][14] and [Ru^{III}(dpm)$_3$] (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate)[15] were synthesized by the literature methods with some modification.[16] [Ru(acac)$_3$] and [Ru(dpm)$_3$] were purified by chromatography on alumina (Merck alumina 90) columns using benzene as

(1) Dwyer, F. P.; Gyarfas, E. C. *Nature (London)* **1951**, *168*, 29.
(2) Moeller, T.; Gulyas, E. *J. Inorg. Nucl. Chem.* **1958**, *5*, 245.
(3) Collman, J. P.; Blair, R. P.; Marshall, R. L.; Slade, L. *Inorg. Chem.* **1963**, *2*, 576.
(4) Fay, R. C.; Girgis, A. Y.; Klabunde, U. *J. Am. Chem. Soc.* **1970**, *92*, 7056.
(5) (a) Nordén, B. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 387. (b) Nordén, B.; Jonás, I. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 33. (c) Jonás, I.; Nordén, B. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 43.
(6) Čelap, M. B.; Hodzic, I. M.; Janjic, T. J. *J. Chromatogr.* **1980**, *198*, 172.
(7) (a) Yamamoto, M.; Iwamoto, E.; Kozasa, A.; Takemoto, K.; Yamamoto, Y.; Tatehara, A. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 71. (b) Yamagishi, A. *J. Chem. Soc., Chem. Commun.* **1981**, *1168*. (c) Yamagishi, A.; Ohnishi, R.; Soma, M. *Chem. Lett.* **1982**, *85*. (d) Yamagishi, A. *Inorg. Chem.* **1982**, *21*, 3393.
(8) Mason, S. F.; Peacock, R. D.; Prosperi, T. *J. Chem. Soc., Dalton Trans.* **1977**, 702.
(9) Drake, A. F.; Gould, J. M.; Mason, S. F.; Rosini, C.; Woodley, F. J. *Polyhedron* **1983**, *2*, 537.
(10) (a) Okamoto, Y.; Honda, S.; Yashima, E.; Yuki, H. *Chem. Lett.* **1983**, 1221. (b) Okamoto, Y.; Yashima, E.; Hatada, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1051.
(11) Okamoto, Y.; Honda, S.; Okamoto, I.; Yuki, H.; Murata, S.; Noyori, R.; Takaya, H. *J. Am. Chem. Soc.* **1981**, *103*, 6971.
(12) Larsen, E.; Mason, S. F.; Searle, G. H. *Acta Chem. Scand.* **1966**, *20*, 191.
(13) Mason, S. F. *Inorg. Chim. Acta Rev.* **1968**, 89.
(14) Wilkinson, G. *J. Am. Chem. Soc.* **1952**, *74*, 6146.
(15) Patterson, G. S.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2285.
(16) Endo, A.; Shimizu, K.; Sato, G. P.; Mukaida, M. *Chem. Lett.* **1984**, 437.

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