spectroscopy) of $(CF_3)_2POH^2$ and $(CF_3)_2P(O)C(CH_3)_3{}^2$ (0.067 g, 0.16 mmol of each component).

**Reaction of $(CF_3)_2POH$ with $(CH_3)_3Cl$.** $(CF_3)_2POH^2$ (0.101 g, 0.54 mmol) was allowed to react with excess $(CH_3)_3CCl$ for 4 days at 70 °C. Vacuum fractionation gave a mixture of $(CF_3)_2POH$ and $(CF_3)_2P(O)C(CH_3)_3$ (0.094 g), HCl (0.015 g, 0.41 mmol), and unreacted $(CH_3)_3Cl$.

**Thermal Stability of $(CF_3)_2POC(CH_3)_3$.** A sample of $(CF_3)_2POC(CH_3)_3$ was quantitatively recovered unchanged after heating at 70 °C for 5 h.

**Treatment of $(CF_3)_2POC(CH_3)_3$ with $(CH_3)_3CCl$.** A sample of $(CF_3)_2POC(CH_3)_3$ ($\sim$1 mmol) was combined with an equal molar quantity of $(CH_3)_3CCl$ in a 5-mm o.d. NMR tube. Examination by $^1H$ and $^{19}F$ NMR spectroscopy after 2 days at room temperature showed that no detectable rearrangement had occurred. The mixture was heated to 70 °C for 2 days but again, according to the NMR spectra, no rearrangement had occurred.

**Treatment of $(CF_3)_2POC(CH_3)_3$ with $CH_3I$.** Approximately equimolar quantities of $(CF_3)_2POC(CH_3)_3$ ($\sim$1 mmol) and $CH_3I$ showed no sign of rearrangement after 2 weeks at 25 °C according to NMR spectroscopy.

**Reaction of $(CF_3)_2PCl$ with Benzyl Alcohol.** $(CF_3)_2PCl^{16}$ (0.190 g, 0.93 mmol) and benzyl alcohol (0.14 g, 1.3 mmol) were heated at 70 °C for 4 h. Vacuum fractionation gave $(CF_3)_2POH^2$ (0.115 g, 0.62 mmol) and an oil of low volatility which was not identified.

**Reaction of $(CH_3)_3CI$ with $(CH_3)_3N$.** $(CH_3)_3CI$ (0.295 g, 1.61 mmol) and $(CH_3)_3N$ (0.096 g, 1.60 mmol) reacted slowly at room temperature, and rapidly at 100 °C. Vacuum fractionation after 24 h of reaction at 100 °C gave $(CH_3)_2C{=}CH_2$ (0.071 g, 1.27 mmol) and a trace of starting materials. The NMR spectrum of the white involatile salt showed only signals due to $(CH_3)_3NH^+I^-$.

**Acknowledgment.** We thank the National Research Council of Canada for financial support of this work.

**Registry No.** $(CF_3)_2POCH_3$, 684-25-3; $(CF_3)_2POC_2H_5$, 1692-49-5; $(CF_3)_2POCH(CH_3)_2$, 71009-82-0; $(CF_3)_2POC(CH_3)_3$, 4571-88-4; $(CF_3)_2PSCH_2CH_3$, 71009-83-1; $(CF_3)_2PSCH(CH_3)_2$, 71009-84-2; $(CF_3)_2PSC(CH_3)_3$, 1733-46-6; $(CF_3)_2P(O)OCH_2CH_3$, 71009-85-3; $(CF_3)_2P(O)OCH(CH_3)_2$, 71009-86-4; $(CF_3)_2P(O)SCH_3$, 71009-87-5; $(CF_3)_2P(O)SCH_2CH_3$, 71009-88-6; $(CF_3)_2P(O)SCH(CH_3)_2$, 71009-89-7; $(CF_3)_2P(S)OCH_3$, 71040-58-9; $(CF_3)_2P(S)OCH_2CH_3$, 71009-90-0; $(CF_3)_2P(S)OCH(CH_3)_2$, 71009-91-1; $(CF_3)_2P(S)SCH_3$, 18799-79-6; $(CF_3)_2P(S)SCH_2CH_3$, 71009-92-2; $(CF_3)_2P(S)SCH(CH_3)_2$, 71009-93-3; $(CF_3)_2P(S)SC(CH_3)_3$, 71009-94-4; $(CF_3)_2P(O)C(CH_3)_3$, 71040-59-0; $(CF_3)_2PP(CF_3)_2$, 2714-60-5; $(CF_3)_2PS_2H$, 18799-75-2; $(CH_3)_3CI$, 558-17-8; $(CF_3)_2P(S)OH$, 35814-49-4; $(CF_3)_2P(S)OC(CH_3)_3$, 71009-95-5; $(CF_3)_2P(O)Cl$, 646-71-9; $(CH_3)_3NH^+(CF_3)_2PSO^-$, 71009-96-6; $(CF_3)_2P(O)N(CH_3)_2$, 3331-12-2; $(CF_3)_2P(S)Cl$, 18799-82-1; $(CF_3)_2P(S)N(CH_3)_2$, 18799-80-9; $(CF_3)_2PCl$, 650-52-2; $(CF_3)_2POH$, 359-65-9; $(CH_3)_2CHOH$, 67-63-0; $(CH_3)_3COH$, 75-65-0; $(CH_3)_3CCl$, 513-36-0; $(CH_3)_3CSH$, 75-66-1; $(CH_3)_2C{=}CH_2$, 115-11-7; $CH_3OH$, 67-56-1; $CH_3CH_2SH$, 75-08-1; $(CH_3)_2CHSH$, 75-33-2; $CH_3CH_2OH$, 64-17-5; $CH_3SH$, 74-93-1; $(CH_3)_3N$, 75-50-3; benzyl alcohol, 100-51-6.

## References and Notes

(1) H. J. Emelêus and J. D. Smith, *J. Chem. Soc.*, 375 (1959).
(2) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).
(3) K. Gosling and A. B. Burg, *J. Am. Chem. Soc.*, **87**, 2113 (1965).
(4) R. G. Cavell and H. J. Emelêus, *J. Chem. Soc.*, 5825 (1964).
(5) A. B. Burg and I. B. Mishra, *Inorg. Chem.*, **8**, 1199 (1969).
(6) A. B. Burg and D. K. Kang, *J. Am. Chem. Soc.*, **92**, 1901 (1970).
(7) A. A. Pinkerton and R. G. Cavell, *J. Am. Chem. Soc.*, **93**, 2384 (1971).
(8) H. J. Emelêus, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 563 (1955).
(9) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, **10**, 2720 (1971).
(10) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Am. Chem. Soc.*, **90**, 2015 (1968).
(11) K. Gosling and A. B. Burg, *J. Am. Chem. Soc.*, **90**, 2011 (1968).
(12) F. W. Bennett, H. J. Emelêus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).
(13) K. J. Packer, *J. Chem. Soc.*, 960 (1963).
(14) J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy", Pergamon, London, 1965.
(15) R. Couper and D. R. Stranks, "Techniques of Inorganic Chemistry", Vol VI, H. B. Jonassen and A. Weissberger, Eds., Wiley, New York, 1966, p 6.
(16) A. B. Burg and J. F. Nixon, *J. Am. Chem. Soc.*, **86**, 356 (1964).
(17) A. B. Burg and A. J. Sarkis, *J. Am. Chem. Soc.*, **87**, 238 (1965).

---

Contribution from the Department of Chemistry,
University of Massachusetts, Amherst, Massachusetts 01003

# Transition-Metal Eight-Coordination. 13. Synthesis, Characterization, and Crystal and Molecular Structure of the Schiff-Base Chelate Bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV) Benzene Solvate

RONALD D. ARCHER,* ROBERTA O. DAY, and MARVIN L. ILLINGSWORTH

*Received February 21, 1979*

As part of our program to elucidate eight-coordinate complexes and their polymeric counterparts we have isolated and structurally characterized the model Schiff-base chelate bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV), $Zr(dsp)_2$, as the benzene solvate $Zr(dsp)_2 \cdot 2.5C_6H_6$. The synthesis involves a condensation between tetrakis(salicylaldehydato)zirconium(IV), $Zr(sal)_4$, and *o*-phenylenediamine, a method which also allows the synthesis of analogous coordination polymers. The $Zr(dsp)_2$ unit is an eight-coordinate dodecahedral species with nitrogen donors in the dodecahedral A position and oxygen donors in the B positions in accord with theoretical predictions. The chelating ligands span the *mam* edges. The Zr–O bonds average 2.10 Å, which is appreciably shorter than the Zr–N distance of 2.43 Å. The donor atoms are in an almost perfect dodecahedral array with the trapezoidal planes intersecting at 89.2°, even though the chelating ligands are quite puckered from these planes. The $Zr(dsp)_2 \cdot 2.5C_6H_6$ solvate crystallizes in the space group $P\bar{1}$ with $Z = 2$, $a = 13.037$ (4) Å, $b = 13.669$ (6) Å, $c = 14.500$ (2) Å, $\alpha = 98.81$ (2)°, $\beta = 116.47$ (2)°, and $\gamma = 92.78$ (3)°.

## Introduction

The monomeric Schiff-base chelate bis(*N*,*N*′-disalicylidene-1,2-phenylenediamino)zirconium(IV), $Zr(dsp)_2$, has been synthesized and characterized as a model for analogous polymers, which have been prepared[1] as part of a program to develop tractable, thermally stable coordination polymers containing nonrigid metal centers. The molecular structure of the benzene solvate has been determined by means of single-crystal X-ray diffraction analysis in order to learn the detailed disposition of two quadridentate Schiff-base ligands about a $d^0$ metal ion. Previous structural studies[2] with this ligand for lower coordination numbers have shown that the ligand can coordinate in either a planar or a nonplanar fashion.

0020-1669/79/1318-2908$01.00/0

Of particular concern were the positioning of the donor atoms about the metal and the flexibility allowed the remainder of the chelating ligand. As is evident from this study, the donor atoms position themselves according to the $d^0$ extension of Orgel's rule for eight-coordinate species,[3] even though the ligands themselves are quite skewed from the trapezoidal planes occupied by the donor atoms.

## Experimental Section

**Reagents.** Reagent grade or equivalent solvents and chemicals were used. Tetrakis(2,4-pentanedionato)zirconium(IV), $Zr(acac)_4$, was either purchased from Alfa-Ventron or prepared from zirconyl chloride via the procedure of Young and Arch.[4] The compound was recrystallized from benzene/petroleum ether (bp 61–70 °C) prior to use. Salicylaldehyde was distilled under reduced pressure prior to its use in the synthesis of $Zr(sal)_4$. Nitrogen atmospheres were used in the presence of free amines or the easily hydrolyzable $Zr(sal)_4$.

***N,N'*-Disalicylidene-1,2-phenylenediamine.** The Schiff base was synthesized according to previously published procedures;[5] mp 165–166 °C (uncor). Anal. Calcd for $C_{20}H_{16}N_2O_2$: C, 76.0; H, 5.10; N, 8.87. Found: C, 75.8; H, 5.22; N, 9.05.

**Tetrakis(salicylaldehydato)zirconium(IV), $Zr(sal)_4$.**[6] This pale yellow solid compound was prepared from 2.69 g (5.5 mmol) of recrystallized $Zr(acac)_4$, mp 194–195 °C, dissolved in 60 mL (0.57 mol) of salicylaldehyde, and slowly distilled under reduced pressure (51 °C, 2–3 torr, 72 h). Filtration under nitrogen and multiple petroleum ether (bp 61–70 °C) washes produced 3.02 g of product; >95% yield; mp 208–209 °C (uncor). Anal. Calcd for $C_{28}H_{20}O_8Zr$: C, 58.5; H, 3.51. Found: C, 58.8; H, 3.57.

**Tetrakis(3-methoxysalicylaldehydato)zirconium(IV).** $Zr(acac)_4$ (3.8 g, 7.9 mmol) was dissolved under nitrogen in 48.5 g (319 mmol) of hot (53 °C) 3-methoxysalicylaldehyde, which had been recrystallized from petroleum ether. The clear orange solution was slowly evacuated, and we proceeded as with the parent compound. After 3 days the hot reaction mixture was filtered, washed several times with petroleum ether (bp 61–70 °C), and dried under a stream of nitrogen. The light yellow powder was produced, mp 205–206 °C (uncor), in essentially quantitative yield. Anal. Calcd for $C_{32}H_{28}O_{12}Zr$: C, 55.3; H, 4.03; Zr, 13.1. Found: C, 55.2; H, 3.73; Zr, 13.1.

**Bis(*N,N'*-disalicylidene-1,2-phenylenediamino)zirconium(IV), $Zr(dsp)_2$.**[6] **Method A.** The addition of a solution of 0.216 g (2.00 mmol) of 1,2-phenylenediamine in 30 mL of $CH_2Cl_2$ to a solution of 0.575 g (1.00 mmol) of $Zr(sal)_4$ in 70 mL of $CH_2Cl_2$ produced bright yellow $Zr(dsp)_2$ in over 70% yield after heating the solution for 1 h under reflux conditions, concentrating to about 20 mL, adding petroleum ether dropwise until a precipitate formed, cooling, filtering, and recrystallizing from benzene/petroleum ether (bp 61–70 °C).

**Method B.** A solution of 1.90 g of $H_2dsp$ (6.0 mmol) in 600 mL of absolute ethanol under nitrogen was added to a solution of 0.97 g of zirconyl chloride (3.0 mmol) in 150 mL of absolute ethanol under $N_2$. A solution of 3.6 g of urea (60 mmol) in 250 mL of nitrogen-swept absolute ethanol was added. The cloudy solution was heated to the boiling point, and a yellow precipitate occurred. After the solution was heated under reflux conditions for 2.5 days, the yellow precipitate was filtered and air-dried; yield 1.6 g, >70%. Recrystallization was accomplished from benzene/petroleum ether.

Thorough drying at 100 °C in vacuo for several days produced the anhydrous product. Anal. Calcd for $C_{40}H_{28}N_4O_4Zr$: C, 66.8; H, 3.92; N, 7.79; Zr, 12.7. Found: C, 67.0; H, 3.94; N, 7.76; Zr, 12.8.

**Crystal Growth.** Crystals for X-ray analysis were grown from saturated benzene/petroleum ether (bp 61–70 °C) solution of recrystallized $Zr(dsp)_2$. Crystals from pure benzene solutions were often very soft, and suitable crystals were not obtained from either THF or $CH_2Cl_2$ solutions.

**Spectral Studies.** Infrared spectra were obtained as KBr mulls with a Perkin-Elmer Model 180 spectrometer and calibrated against polystyrene. Nuclear magnetic resonance spectra were obtained in deuterated solvents with a Perkin-Elmer Model R12 spectrometer; the tetramethylsilane reference was at $\tau$ 10.00. Ultraviolet and visible absorption spectra were obtained in solution in 1-cm matched cells with a Hitachi Model EPS-3T spectrophotometer. Mass spectral data for the zirconium complexes were recorded on a Hitachi Model RMU6L spectrometer and calibrated with perfluorokerosene.

**Table I.** Atomic Coordinates for Nonhydrogen Atoms[a]

| atom type[b] | fractional coordinates | | |
|---|---|---|---|
| | $10^4x$ | $10^4y$ | $10^4z$ |
| Zr | 4992.0 (1) | 7242.4 (1) | 7408.1 (1) |
| OA | 4109 (1) | 7256 (1) | 8326 (1) |
| OB | 6558 (1) | 7679 (1) | 7418 (1) |
| OC | 5044 (1) | 5705 (1) | 7244 (1) |
| OD | 4132 (1) | 8413 (1) | 6755 (1) |
| NA | 3010 (1) | 6493 (1) | 6190 (1) |
| NB | 4690 (1) | 6761 (1) | 5635 (1) |
| NC | 6477 (1) | 6959 (1) | 9069 (1) |
| ND | 5892 (1) | 8762 (1) | 8747 (1) |
| C1 | 3753 (1) | 5992 (1) | 4968 (1) |
| C2 | 2863 (1) | 5866 (1) | 5246 (1) |
| C3 | 1953 (1) | 5103 (1) | 4647 (1) |
| C4 | 1933 (1) | 4472 (1) | 3792 (1) |
| C5 | 2814 (1) | 4586 (1) | 3535 (1) |
| C6 | 3730 (1) | 5337 (1) | 4122 (1) |
| CA | 2089 (1) | 6665 (1) | 6290 (1) |
| CA1 | 3069 (1) | 7367 (1) | 8232 (1) |
| CA2 | 2063 (1) | 7124 (1) | 7240 (1) |
| CA3 | 980 (1) | 7256 (1) | 7196 (1) |
| CA4 | 860 (1) | 7593 (1) | 8079 (1) |
| CA5 | 1837 (1) | 7793 (1) | 9042 (1) |
| CA6 | 2922 (1) | 7696 (1) | 9126 (1) |
| CB | 5244 (1) | 7157 (1) | 5193 (1) |
| CB1 | 6944 (1) | 8044 (1) | 6832 (1) |
| CB2 | 6304 (1) | 7837 (1) | 5730 (1) |
| CB3 | 6757 (1) | 8232 (1) | 5122 (1) |
| CB4 | 7824 (1) | 8814 (1) | 5599 (1) |
| CB5 | 8446 (1) | 9021 (1) | 6689 (1) |
| CB6 | 8022 (1) | 8637 (1) | 7296 (1) |
| C7 | 7368 (1) | 7784 (1) | 9665 (1) |
| C8 | 7062 (1) | 8726 (1) | 9489 (1) |
| C9 | 7906 (1) | 9561 (1) | 9966 (1) |
| C10 | 9040 (1) | 9445 (1) | 10630 (1) |
| C11 | 9329 (1) | 8519 (2) | 10807 (1) |
| C12 | 8502 (1) | 7681 (1) | 10325 (1) |
| CC | 6498 (1) | 6165 (1) | 9466 (1) |
| CC1 | 5050 (1) | 5034 (1) | 7814 (1) |
| CC2 | 5753 (1) | 5233 (1) | 8917 (1) |
| CC3 | 5739 (1) | 4492 (1) | 9488 (1) |
| CC4 | 5024 (1) | 3588 (1) | 8986 (1) |
| CC5 | 4351 (1) | 3403 (1) | 7902 (1) |
| CC6 | 4371 (1) | 4100 (1) | 7328 (1) |
| CD | 5410 (1) | 9546 (1) | 8856 (1) |
| CD1 | 3686 (1) | 9147 (1) | 7087 (1) |
| CD2 | 4285 (1) | 9720 (1) | 8120 (1) |
| CD3 | 3787 (1) | 10531 (1) | 8426 (1) |
| CD4 | 2717 (2) | 10736 (1) | 7757 (1) |
| CD5 | 2128 (1) | 10151 (1) | 6751 (1) |
| CD6 | 2602 (1) | 9391 (1) | 6415 (1) |
| CS1 | 8527 (2) | 5861 (2) | 3253 (2) |
| CS2 | 9066 (2) | 5731 (2) | 2620 (2) |
| CS3 | 9809 (2) | 6510 (3) | 2699 (2) |
| CS4 | 10030 (2) | 7394 (2) | 3386 (3) |
| CS5 | 9494 (2) | 7498 (2) | 4027 (2) |
| CS6 | 8762 (2) | 6743 (2) | 3948 (2) |
| CT1 | 2747 (1) | 7509 (1) | 2897 (1) |
| CT2 | 3149 (1) | 7659 (1) | 2202 (1) |
| CT3 | 3765 (1) | 8555 (1) | 2354 (1) |
| CT4 | 4004 (2) | 9290 (1) | 3175 (1) |
| CT5 | 3626 (1) | 9146 (1) | 3883 (1) |
| CT6 | 3002 (2) | 8253 (1) | 3759 (1) |
| CU1 | 8875 (2) | 4961 (1) | 9272 (2) |
| CU2 | 9737 (1) | 5546 (2) | 9243 (1) |
| CU3 | 10853 (1) | 5572 (1) | 9966 (1) |

[a] Numbers in parentheses are the estimated standard deviation in the last significant figure. [b] Atoms of the chelate are labeled to agree with Figure 1. The 2.5 independent benzene molecules are CS1 through CS6, CT1 through CT6, and CU1 through CU3.

**Space Group Determination and Data Collection.** The crystals deteriorated overnight when removed from the mother liquor, presumably due to loss of benzene from the crystalline solvate. A crystal having approximate dimensions of 0.20 mm × 0.30 mm × 0.40 mm was cut from the tip of a larger lathe immediately after removal from the mother liquor. The crystal was quickly wedged into a thin-walled glass capillary which was sealed with a flame to prevent deterioration

**Table II.** Thermal Parameters for Nonhydrogen Atoms[a]

| atom type[b] | anisotropic parameters | | | | | | $B$,[c] Å² |
|---|---|---|---|---|---|---|---|
| | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ | |
| Zr | 2.52 (1) | 2.88 (1) | 2.43 (1) | 0.31 (1) | 1.15 (1) | 0.19 (1) | 2.62 |
| OA | 3.22 (4) | 5.23 (5) | 3.27 (4) | 0.63 (3) | 1.77 (3) | 0.61 (3) | 3.68 |
| OB | 3.10 (4) | 4.57 (4) | 3.44 (4) | −0.28 (3) | 1.62 (3) | 0.01 (3) | 3.64 |
| OC | 3.97 (4) | 3.34 (4) | 3.28 (4) | 0.57 (3) | 1.66 (3) | 0.54 (3) | 3.53 |
| OD | 4.71 (4) | 3.69 (4) | 3.51 (4) | 1.27 (3) | 1.65 (4) | 0.73 (3) | 3.93 |
| NA | 2.89 (4) | 4.58 (5) | 3.14 (5) | 0.03 (4) | 1.26 (4) | 0.26 (4) | 3.56 |
| NB | 3.19 (4) | 3.63 (5) | 2.42 (4) | 0.46 (4) | 1.23 (4) | 0.03 (4) | 3.08 |
| NC | 3.19 (5) | 4.53 (5) | 2.95 (5) | 1.02 (4) | 1.18 (4) | 0.58 (4) | 3.54 |
| ND | 3.98 (5) | 3.44 (5) | 3.07 (5) | −0.18 (4) | 1.57 (4) | −0.23 (4) | 3.53 |
| C1 | 3.2 (1) | 3.6 (1) | 2.4 (1) | 0.5 (1) | .9 (1) | 0.2 (1) | 3.2 |
| C2 | 3.4 (1) | 4.0 (1) | 2.6 (1) | −0.1 (1) | .8 (1) | −0.1 (1) | 3.5 |
| C3 | 4.2 (1) | 6.5 (1) | 4.3 (1) | −0.9 (1) | 2.0 (1) | −0.7 (1) | 4.9 |
| C4 | 5.0 (1) | 5.9 (1) | 4.7 (1) | −1.4 (1) | 1.8 (1) | −0.9 (1) | 5.3 |
| C5 | 4.8 (1) | 4.5 (1) | 3.6 (1) | 0.5 (1) | 1.6 (1) | −0.2 (1) | 4.4 |
| C6 | 3.8 (1) | 4.2 (1) | 3.2 (1) | 0.7 (1) | 1.5 (1) | 0.5 (1) | 3.7 |
| CA | 2.6 (1) | 5.5 (1) | 3.7 (1) | 0.1 (1) | 1.1 (1) | 0.5 (1) | 4.0 |
| CA1 | 3.4 (1) | 3.3 (1) | 3.8 (1) | 0.4 (1) | 2.1 (1) | 0.9 (1) | 3.3 |
| CA2 | 3.1 (1) | 4.1 (1) | 3.8 (1) | 0.4 (1) | 1.7 (1) | 0.5 (1) | 3.6 |
| CA3 | 3.3 (1) | 6.3 (1) | 4.8 (1) | 0.6 (1) | 1.8 (1) | 0.5 (1) | 4.7 |
| CA4 | 4.0 (1) | 5.6 (1) | 6.6 (1) | 0.9 (1) | 3.3 (1) | 0.7 (1) | 4.8 |
| CA5 | 5.4 (1) | 4.1 (1) | 5.6 (1) | 0.6 (1) | 3.8 (1) | 0.3 (1) | 4.4 |
| CA6 | 4.2 (1) | 4.6 (1) | 4.0 (1) | 0.6 (1) | 2.3 (1) | 0.6 (1) | 4.1 |
| CB | 4.1 (1) | 3.8 (1) | 2.8 (1) | 0.8 (1) | 1.8 (1) | 0.4 (1) | 3.4 |
| CB1 | 3.0 (1) | 3.4 (1) | 4.3 (1) | 0.5 (1) | 2.2 (1) | 0.4 (1) | 3.3 |
| CB2 | 4.1 (1) | 3.4 (1) | 3.7 (1) | 0.4 (1) | 2.3 (1) | 0.4 (1) | 3.5 |
| CB3 | 4.9 (1) | 4.9 (1) | 4.7 (1) | 0.4 (1) | 2.6 (1) | 1.1 (1) | 4.6 |
| CB4 | 5.6 (1) | 6.3 (1) | 6.3 (1) | 0.2 (1) | 3.6 (1) | 1.9 (1) | 5.4 |
| CB5 | 4.5 (1) | 6.3 (1) | 6.2 (1) | −0.6 (1) | 2.6 (1) | 1.0 (1) | 5.4 |
| CB6 | 3.7 (1) | 5.6 (1) | 4.7 (1) | 0.1 (1) | 2.1 (1) | 0.5 (1) | 4.5 |
| C7 | 3.1 (1) | 5.1 (1) | 2.8 (1) | −0.2 (1) | .5 (1) | −0.2 (1) | 3.9 |
| C8 | 3.5 (1) | 4.6 (1) | 3.2 (1) | −0.4 (1) | 1.1 (1) | −0.7 (1) | 3.9 |
| C9 | 5.4 (1) | 5.1 (1) | 5.6 (1) | −0.8 (1) | 1.9 (1) | −0.8 (1) | 5.6 |
| C10 | 4.9 (1) | 7.8 (1) | 6.4 (1) | −1.8 (1) | 1.3 (1) | −1.5 (1) | 6.5 |
| C11 | 4.0 (1) | 8.8 (1) | 6.2 (1) | −0.3 (1) | .1 (1) | −0.6 (1) | 6.6 |
| C12 | 4.1 (1) | 6.7 (1) | 4.9 (1) | 0.7 (1) | .6 (1) | 0.2 (1) | 5.6 |
| CC | 3.8 (1) | 6.0 (1) | 2.9 (1) | 1.7 (1) | 1.1 (1) | 1.2 (1) | 4.0 |
| CC1 | 3.7 (1) | 3.6 (1) | 4.4 (1) | 1.3 (1) | 2.3 (1) | 0.9 (1) | 3.5 |
| CC2 | 3.9 (1) | 4.2 (1) | 4.2 (1) | 1.2 (1) | 2.1 (1) | 1.4 (1) | 3.9 |
| CC3 | 6.0 (1) | 5.9 (1) | 4.9 (1) | 1.9 (1) | 2.9 (1) | 2.2 (1) | 5.1 |
| CC4 | 7.1 (1) | 5.5 (1) | 7.9 (1) | 2.0 (1) | 4.5 (1) | 3.5 (1) | 5.7 |
| CC5 | 6.6 (1) | 4.1 (1) | 7.4 (1) | 0.4 (1) | 3.8 (1) | 1.6 (1) | 5.5 |
| CC6 | 5.1 (1) | 3.9 (1) | 5.5 (1) | 0.3 (1) | 2.6 (1) | 0.8 (1) | 4.7 |
| CD | 5.2 (1) | 3.4 (1) | 3.9 (1) | 0.0 (1) | 2.6 (1) | −0.4 (1) | 3.9 |
| CD1 | 4.7 (1) | 3.6 (1) | 4.1 (1) | 1.0 (1) | 2.6 (1) | 1.3 (1) | 3.8 |
| CD2 | 5.0 (1) | 3.3 (1) | 4.4 (1) | 0.8 (1) | 3.0 (1) | 0.9 (1) | 3.8 |
| CD3 | 7.1 (1) | 4.4 (1) | 4.8 (1) | 1.1 (1) | 3.7 (1) | 0.9 (1) | 4.9 |
| CD4 | 8.2 (1) | 5.8 (1) | 7.0 (1) | 3.6 (1) | 5.0 (1) | 2.3 (1) | 5.6 |
| CD5 | 6.6 (1) | 7.5 (1) | 6.1 (1) | 3.5 (1) | 3.3 (1) | 2.8 (1) | 6.0 |
| CD6 | 5.9 (1) | 5.3 (1) | 4.8 (1) | 2.5 (1) | 2.3 (1) | 1.8 (1) | 5.0 |
| CS1 | 7.6 (1) | 9.7 (2) | 11.4 (2) | 1.7 (1) | 5.1 (1) | 3.2 (1) | 8.8 |
| CS2 | 8.0 (1) | 12.1 (2) | 8.6 (1) | 3.6 (1) | 3.8 (1) | 2.5 (1) | 9.1 |
| CS3 | 9.4 (2) | 18.7 (3) | 11.5 (2) | 2.7 (2) | 6.8 (2) | 6.3 (2) | 10.7 |
| CS4 | 7.5 (2) | 13.5 (2) | 16.3 (3) | 0.3 (2) | 4.9 (2) | 6.7 (2) | 11.0 |
| CS5 | 6.6 (1) | 9.7 (2) | 10.7 (2) | 1.9 (1) | 3.5 (1) | 3.3 (1) | 8.7 |
| CS6 | 6.9 (1) | 8.9 (1) | 11.1 (2) | 1.7 (1) | 5.0 (1) | 2.3 (1) | 8.3 |
| CT1 | 5.8 (1) | 7.4 (1) | 8.8 (1) | 0.3 (1) | 3.2 (1) | 2.3 (1) | 7.1 |
| CT2 | 8.2 (1) | 7.4 (1) | 5.8 (1) | −0.7 (1) | 2.9 (1) | 0.1 (1) | 7.2 |
| CT3 | 10.9 (2) | 9.0 (1) | 8.3 (1) | −0.5 (1) | 5.5 (1) | 2.3 (1) | 8.5 |
| CT4 | 9.1 (1) | 5.4 (1) | 13.3 (2) | −0.4 (1) | 5.8 (2) | 1.2 (1) | 8.4 |
| CT5 | 7.5 (1) | 7.2 (1) | 9.8 (2) | 1.6 (1) | 3.3 (1) | −2.2 (1) | 7.9 |
| CT6 | 7.4 (1) | 10.9 (2) | 7.5 (1) | 3.3 (1) | 4.6 (1) | 2.6 (1) | 7.5 |
| CU1 | 6.2 (1) | 8.3 (1) | 6.0 (1) | 0.7 (1) | 2.1 (1) | 0.1 (1) | 7.1 |
| CU2 | 9.2 (1) | 8.2 (1) | 6.5 (1) | 0.3 (1) | 2.7 (1) | 2.5 (1) | 7.9 |
| CU3 | 7.8 (1) | 8.4 (1) | 7.1 (1) | −2.1 (1) | 3.7 (1) | 0.3 (1) | 7.4 |

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; the $B_{ij}$ in Å² are related to the dimensionless $\beta_{ij}$ employed during refinement as $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$. [b] See footnote *b* in Table I. [c] Equivalent isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

by loss of benzene. Preliminary investigations using an Enraf-Nonius CAD4 automated diffractometer and graphite-monochromated molybdenum radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle = 3.1°, $\lambda(K\alpha_1) = 0.709\,30$ Å, $\lambda(K\alpha_2) = 0.713\,59$ Å) showed triclinic ($\bar{1}$) symmetry, consonant with either space group $P1$ or $P\bar{1}$. The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.52° \leq \theta_{\mathrm{MoK}\bar{\alpha}} \leq 13.35°$ and as measured at an ambient laboratory temperature of 23 ± 2 °C are $a = 13.037$ (4) Å, $b = 13.669$ (6) Å, $c = 14.500$ (2) Å, $\alpha = 98.81$ (2)°, $\beta = 116.47$ (2)°, and $\gamma = 92.78$ (3)°. A unit cell content of two molecules of the Zr complex and five molecules of benzene gives a calculated density of 1.341 g/cm³ in agreement with the observed

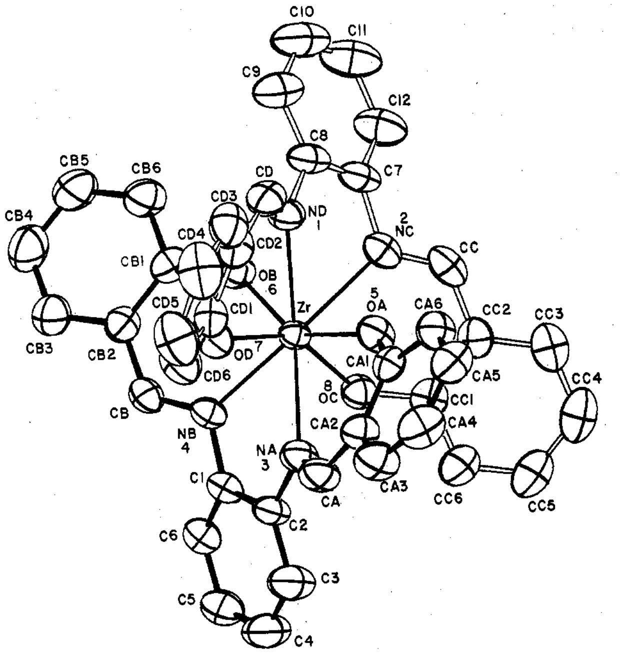


**Figure 1.** ORTEP plot showing the $Zr(dsp)_2$ atom numbering scheme and molecular structure viewed down the pseudo twofold axis, which is coincident with one of the twofold axes of the $\bar{4}2m$ ($D_{2d}$) donor symmetry; cf. Figure 4. Thermal ellipsoids are at the 50% probability level. The numbers 1–8 are used in defining the $\delta$ dihedral angles.

density of 1.35 g/cm$^3$ as determined by flotation in aqueous KI. The space group $P\bar{1}$ ($C_i^1$-No. 2)[7] was chosen on the assumption that there would be one molecule of the Zr complex in the asymmetric unit. This choice, which implies two molecules of benzene in general positions and one benzene molecule lying on an inversion center, was confirmed by all subsequent stages of solution and refinement.

Data were collected by using the $\theta$–$2\theta$ scan mode with a $\theta$ scan range of $(0.80 + 0.35 \tan \theta)°$ centered about the calculated Mo K$\bar{\alpha}$ peak position. The scan range was actually extended an extra 25% on either side of the aforementioned limits for the measurement of background radiation. The scan rates varied from 1.12 to 4.02° $\theta$/min, the rate to be used for each reflection having been determined by a prescan. The intensity, $I$, for each reflection is then given by $I = (FF/S)(P - 2(B1 + B2))$ where $P$ are the counts accumulated during the peak scan, B1 and B2 are the left and right background counts, $S$ is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, $\sigma_I$, were computed as $\sigma_I^2 = ((FF)^2/S^2)(P + 4(B1 + B2)) + 0.002I^2$. A total of 5176 independent reflections ($+h,\pm k,\pm l$) having $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 43°$ were measured. Five standard reflections, monitored after every 12000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{MoK\bar{\alpha}} = 0.296$ mm$^{-1}$), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

**Solution and Refinement of Structure.** Initial coordinates for 39 of the 64 independent nonhydrogen atoms were obtained by direct methods (MULTAN). Initial coordinates for the remaining independent nonhydrogen atoms were obtained by standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[8] of the structural parameters for these 64 atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.086 and a weighted residual $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$ of 0.093 for the 4485 independent reflections having $I \geq \sigma_I$. Anisotropic refinement employing variable weights ($w^{1/2} = 2F_oLp/\sigma_I$) then gave $R = 0.059$ and $R_w = 0.075$. Coordinates for the 43 independent hydrogen atoms were then inferred from the required geometries of the molecules, using a C–H bond length of 0.98 Å. Because of the size of the structure (107 independent atoms) no attempt was made to refine the parameters for the H atoms, although their positional parameters were updated as refinement converged.

**Table III.** Fixed Parameters for Hydrogen Atoms

| atom type[a] | fractional coordinates $10^4x$ | $10^4y$ | $10^4z$ | $B$,[b] Å$^2$ |
|---|---|---|---|---|
| H3 | 1320 | 5011 | 4831 | 5 |
| H4 | 1284 | 3939 | 3370 | 6 |
| H5 | 2798 | 4135 | 2932 | 5 |
| H6 | 4368 | 5408 | 3943 | 5 |
| HA | 1343 | 6463 | 5660 | 5 |
| HA3 | 287 | 7101 | 6512 | 5 |
| HA4 | 96 | 7691 | 8028 | 5 |
| HA5 | 1757 | 8008 | 9682 | 5 |
| HA6 | 3602 | 7860 | 9819 | 5 |
| HB | 4907 | 6975 | 4425 | 5 |
| HB3 | 6310 | 8091 | 4352 | 5 |
| HB4 | 8138 | 9080 | 5172 | 6 |
| HB5 | 9196 | 9446 | 7031 | 6 |
| HB6 | 8483 | 8779 | 8064 | 5 |
| H9 | 7699 | 10226 | 9833 | 6 |
| H10 | 9635 | 10032 | 10974 | 7 |
| H11 | 10130 | 8447 | 11278 | 7 |
| H12 | 8720 | 7018 | 10452 | 6 |
| HC | 7068 | 6202 | 10200 | 5 |
| HC3 | 6241 | 4616 | 10250 | 5 |
| HC4 | 4993 | 3086 | 9392 | 6 |
| HC5 | 3857 | 2761 | 7544 | 6 |
| HC6 | 3901 | 3946 | 6561 | 5 |
| HD | 5847 | 10062 | 9491 | 5 |
| HD3 | 4218 | 10950 | 9131 | 5 |
| HD4 | 2374 | 11288 | 7984 | 6 |
| HD5 | 1355 | 10285 | 6272 | 6 |
| HD6 | 2179 | 9010 | 5692 | 5 |
| HS1 | 7972 | 5320 | 3206 | 9 |
| HS2 | 8917 | 5096 | 2129 | 9 |
| HS3 | 10197 | 6435 | 2251 | 10 |
| HS4 | 10564 | 7947 | 3421 | 10 |
| HS5 | 9655 | 8125 | 4533 | 9 |
| HS6 | 8379 | 6817 | 4399 | 8 |
| HT1 | 2279 | 6877 | 2787 | 8 |
| HT2 | 2996 | 7129 | 1599 | 8 |
| HT3 | 4043 | 8665 | 1846 | 9 |
| HT4 | 4451 | 9927 | 3264 | 9 |
| HT5 | 3798 | 9683 | 4483 | 8 |
| HT6 | 2741 | 8144 | 4278 | 8 |
| HU1 | 8067 | 4931 | 8743 | 8 |
| HU2 | 9548 | 5947 | 8695 | 8 |
| HU3 | 11466 | 5985 | 9932 | 8 |

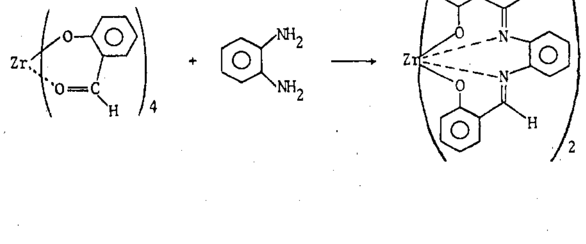
[a] Hydrogen atoms are labeled according to the carbon atom to which they are bonded. [b] $B$ was set equal to 5 Å$^2$ if the last isotropic thermal parameter of the atom to which the H atom is bonded was less than 5 Å$^2$. If the isotropic thermal parameter of the nonhydrogen atom was greater than 5 Å$^2$, $B$ was set equal to the next highest integral value.

Refinement including the hydrogen atoms as fixed isotropic contributions led to the final values of $R = 0.041$, $R_w = 0.049$ and $S$[9] $= 1.55$ for the 4485 reflections having $I \geq \sigma_I$. During the last cycle of refinement the largest shift in any parameter was 0.08 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.53 e/Å$^3$.

Computations were done on a CDC 6600 computer (Model Cyber 74-18) using the direct methods program MULTAN, by Main, Germain, and Woolfson, Zalkin's Fourier program FORDAP, Prewitt's full-matrix least-squares program SFLS, Johnson's thermal ellipsoid plot program ORTEP, and several locally written programs.

## Results

**Synthesis.** The reaction of stoichiometric amounts of freshly



(1)

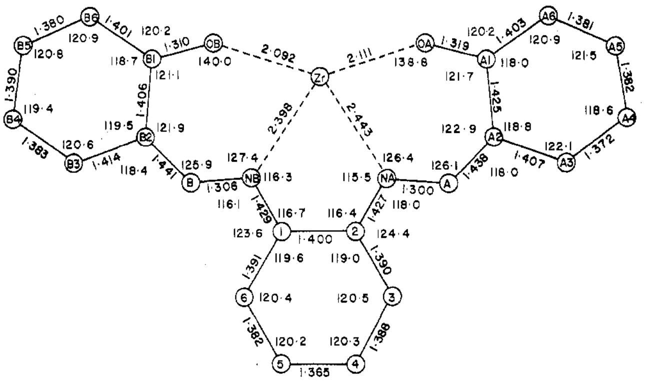


**Figure 2.** Bond distances in Å and bond angles in degrees for the AB $dsp^{2-}$ ligand. Esd's are 0.001–0.002 Å and 0.1°.

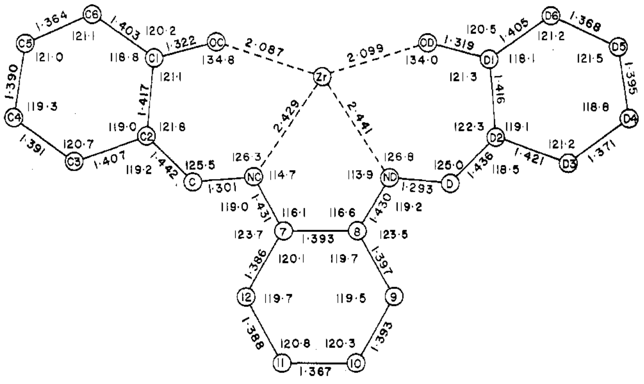


**Figure 3.** Bond distances in Å and bond angles in degrees for the CD $dsp^{2-}$ ligand. Esd's are 0.002–0.003 Å and 0.1–0.2°.

prepared tetrakis(salicylaldehydato)zirconium(IV), $Zr(sal)_4$, with 1,2-phenylenediamine in $CH_2Cl_2$ under $N_2$ produces a bright yellow $Zr(dsp)_2$ product, eq 1.

**Structure of $Zr(dsp)_2 \cdot 2.5C_6H_6$.** The atomic coordinates and the thermal parameters for the nonhydrogen atoms are given in Tables I and II with the numbering system for the chelate shown in Figure 1. The analogous fixed hydrogen atom parameters are given in Table III. The bond lengths and angles of the two independent ligands are given diagrammatically in Figures 2 and 3. The bond lengths and angles around zirconium are given in Table IV.

The benzene solvate molecules are normal with an average C–C bond length of 1.362 (4, 13, 35) Å and an average C–C–C bond angle of 120.0 (3, 9, 23)°.[10] The benzene solvate atoms are labeled S1 to S6, T1 to T6, and U1 to U3 in the tables.

The coordination polyhedron is a trigonal-faced dodecahedron (pseudo $D_{2d}$ or $\bar{4}2m$) with $\theta_A$ and $\theta_B$ values of 33.4 (1, 2, 2) and 73.0 (1, 5, 5)° and M–A (Zr–N) and M–B (Zr–O) values of 2.428 (1, 15, 30) and 2.097 (1, 8, 14) Å, respectively.[11] The dihedral angles between the dodecahedral trapezoidal planes[13] are 89.2° with or without zirconium. The planarity of these trapezoids is indicated in Table V, and the more recently developed $\delta$ and $\phi$ dihedral angles[14] are given in Table VI All parameters point to a dodecahedral geometry with each ligand spanning *mam* edges.[12] The dodecahedral edge values for the $Zr(dsp)_2$ group are summarized in Table VII. Both the actual atomic coordinate and unit vector values are given.

Even though the donor atoms of each ligand are nearly coplanar, the ligands as a whole are quite distorted from planarity as is evident from Figure 4. The relevant torsion angles are listed in Table VIII. The major cause of nonplanarity appears to be rotation about the nitrogen–phenyl bonds, which produces torsion angles averaging 27.4°.

**Table IV.** Bond Lengths and Angles Involving Zr in $Zr(dsp)_2$[a, b]

| Lengths | | | |
|---|---|---|---|
| Zr-OA | 2.111 | Zr-NA | 2.443 |
| Zr-OB | 2.092 | Zr-NB | 2.398 |
| Zr-OC | 2.087 | Zr-NC | 2.429 |
| Zr-OD | 2.099 | Zr-ND | 2.441 |
| **Angles** | | | |
| OA-Zr-OB[c] | 144.9 | OC-Zr-NA | 75.1 |
| OA-Zr-OC | 93.7 | OC-Zr-NB | 77.2 |
| OA-Zr-OD | 89.9 | OC-Zr-NC | 73.2 |
| OA-Zr-NA | 74.3 | OC-Zr-ND | 139.4 |
| OA-Zr-NB | 141.5 | OD-Zr-NA | 74.3 |
| OA-Zr-NC | 77.6 | OD-Zr-NB | 79.7 |
| OA-Zr-ND | 75.9 | OD-Zr-NC | 139.4 |
| OB-Zr-OC | 98.9 | OD-Zr-ND | 73.2 |
| OB-Zr-OD | 96.8 | NA-Zr-NB[c] | 67.1 |
| OB-Zr-NA | 140.6 | NA-Zr-NC | 135.6 |
| OB-Zr-NB | 73.6 | NA-Zr-ND | 135.4 |
| OB-Zr-NC | 75.0 | NB-Zr-NC | 132.2 |
| OB-Zr-ND | 73.3 | NB-Zr-ND | 133.7 |
| OC-Zr-OD[c] | 146.9 | NC-Zr-ND[c] | 66.3 |
| Zr-OA-CA1 | 138.8 | Zr-OD-CD1 | 134.0 |
| Zr-OB-CB1 | 140.0 | Zr-OC-CC1 | 134.8 |
| Zr-NA-C2 | 115.5 | Zr-ND-C8 | 113.9 |
| Zr-NA-CA | 126.4 | Zr-ND-CD | 126.8 |
| Zr-NB-C1 | 116.3 | Zr-NC-C7 | 114.7 |
| Zr-NB-CB | 125.9 | Zr-NC-CC | 126.3 |

[a] Bond lengths in Å and angles in degrees; estimated standard deviations are 0.001 Å and 0.1°. [b] Atoms are labeled to agree with Figure 1. [c] Used to calculate $\theta_A = 33.4°$ and $\theta_B = 73.0°$.

**Table V.** Deviations in Å from the Least-Squares Mean Trapezoidal Planes of the $Zr(dsp)_2$ Coordination Sphere and Dihedral Angles[a]

Deviations from Planes

| | plane I | plane II | | plane III | plane IV |
|---|---|---|---|---|---|
| OA | 0.012 | 0.002 | OC | −0.005 | 0.016 |
| OB | −0.011 | −0.021 | OD | 0.005 | 0.025 |
| NA | −0.017 | −0.022 | NC | 0.007 | 0.017 |
| NB | 0.016 | 0.011 | ND | −0.007 | 0.001 |
| Zr | (0.038) | 0.029 | Zr | (−0.077) | −0.059 |

Dihedral Angles (deg) between Pairs of Planes

| | | | |
|---|---|---|---|
| I, III | 89.2 | I, IV | 89.2 |
| II, IV | 89.2 | II, III | 89.2 |

[a] The best fit for the trapezoidal planes has been determined for the four donor atoms (planes I and III) and for the donor atoms plus Zr (planes II and IV).

**Table VI.** Other Dihedral Angle Parameters for the $Zr(dsp)_2$ Coordination Sphere[a]

| | dihedral angle | atomic coord | unit vectors | DOD | SAP | BCTP |
|---|---|---|---|---|---|---|
| $\delta$ | 1(57)3 | 28.0 | 39.1 | 29.5 | 0.0 | 21.8 |
| | 2(68)4 | 19.6 | 30.1 | 29.5 | 0.0 | 0.0 |
| | 1(67)4 | 22.5 | 33.0 | 29.5 | 52.4 | 48.2 |
| | 2(58)3 | 25.8 | 36.7 | 29.5 | 52.4 | 48.2 |
| $\phi_{av}$ | | 0.8 | 0.7 | 0.0 | 24.5 | 14.1 |

[a] See Drew[14c] for details on these parameters; DOD = $D_{2d}$ dodecahedron; SAP = $D_{4d}$ square of Archimedes antiprism; BCTP = $C_{2v}$ bicapped-trigonal prism or hendecahedron; all values in degrees.

**Spectra.** The spectral properties of the $Zr(sal)_4$ and $Zr(dsp)_2$ chelates relative to their free ligands are collected in Table IX.

## Discussion

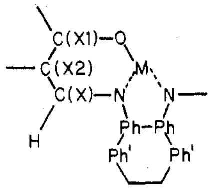
**Synthesis.** The synthesis of the Schiff-base chelate from $Zr(sal)_4$ and phenylenediamine is a straightforward way of avoiding the solubility problems of certain Schiff-base ligands.

**Table VII.** Dodecahedral Edges in the $Zr(dsp)_2$ Unit

| edge[a] | bond length[b] | unit vector[d] | edge[a] | bond length[b] | unit vector[d] |
|---|---|---|---|---|---|
| *a* edges[c] | | | *b* edges | | |
| NA-NB | 2.677 (1) | 1.106 | OA-OC | 3.062 (1) | 1.459 |
| NC-ND | 2.662 (1) | 1.093 | OC-OB | 3.174 (1) | 1.519 |
| mean | 2.670 | 1.100 | OB-OD | 3.134 (1) | 1.496 |
| *g* edges | | | OD-OA | 2.975 (1) | 1.413 |
| NA-OC | 2.774 (1) | 1.208 | mean | 3.086 | 1.472 |
| NA-OD | 2.757 (1) | 1.229 | *m* edges | | |
| NB-OC | 2.807 (1) | 1.247 | NA-OA | 2.764 (1) | 1.208 |
| NB-OD | 2.890 (1) | 1.281 | NB-OB | 2.699 (1) | 1.197 |
| NC-OA | 2.855 (1) | 1.253 | NC-OC | 2.707 (1) | 1.193 |
| NC-OB | 2.765 (1) | 1.217 | ND-OD | 2.721 (1) | 1.193 |
| ND-OA | 2.810 (1) | 1.229 | mean | 2.723 | 1.198 |
| ND-OB | 2.720 (1) | 1.194 | | | |
| mean | 2.797 | 1.231 | *b*/*a* | 1.156 | 1.338 |
| | | | *b*/*m* | 1.133 | 1.229 |
| | | | *b*/*g* | 1.103 | 1.196 |

[a] See Figure 1. [b] In angstroms. [c] Reference 12. [d] HSM (hard sphere model) projects unit vectors (relative to equal M-L distances) $a = m = g = 1.199$ and $b = 1.499$ or $b/a = b/m = b/g = 1.250$; the most favorable polyhedron[12] has $M\text{-}L_A/M\text{-}L_B = 1.03$, $a = m = 1.17$, $g = 1.24$, and $b = 1.49$.

**Table VIII.** Torsion Angles in the dsp Ligands



| torsion angle[a] | *A* | *B* | *C* | *D* | av |
|---|---|---|---|---|---|
| O-C(X1)-C(X2)-C(X) | 5.4 | 4.9 | 0.7 | 0.8 | 3.0 |
| C(X1)-C(X2)-C(X)-N | 6.1 | 8.8 | 11.7 | 14.0 | 10.2 |
| C(X2)-C(X)-N-Ph | 11.6 | 9.1 | 8.1 | 6.0 | 8.7 |
| C(X)-N-Ph-Ph | 24.0 | 27.2 | 29.2 | 29.4 | 27.4 |
| N-Ph-Ph-N | 2.4 | | 0.9 | | 1.6 |

[a] Angles given in degrees; X is used as a general designation of the *A*, *B*, *C*, and *D* parameters; Ph as shown in the structure.

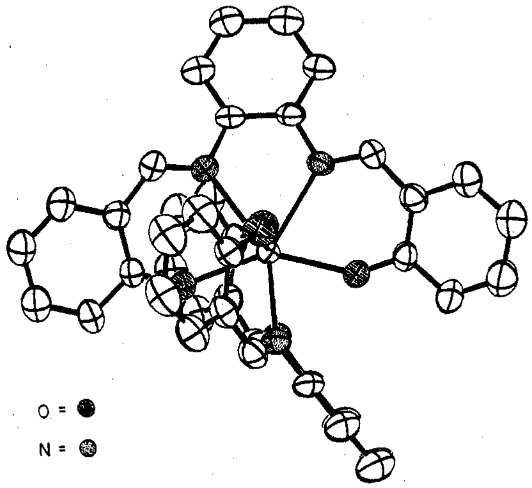


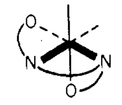
**Figure 4.** ORTEP plot of the structure of $Zr(dsp)_2$ showing the pseudo $\bar{4}2m$ ($D_{2d}$) donor symmetry, the pseudo mirror plane of the ligands, the perpendicular donor trapezoids, and the skewness of the ligands to the trapezoids. Thermal ellipsoids are at the 50% probability level.

For example, whereas Merrell and others[15] have noted solubility difficulty in synthesizing $H_4$tsb chelates (where $tsb^{4-}$ = the tetrakis(*N*,*N*′,*N*″,*N*‴-tetrasalicylidene-1,2,4,5-tetraaminobenzenato anion), we have been able to synthesize zirconium polymers[1] by the analogous reaction between $Zr(sal)_4$ and 1,2,4,5-tetraaminobenzene.

The benzene solvate, $Zr(dsp)_2{\cdot}2.5C_6H_6$, which is readily obtained upon crystallization of $Zr(dsp)_2$ in benzene/petroleum ether solutions, easily loses the solvation molecules, which is indicative of only weak interactions between the chelate and benzene. The structural results substantiate this conclusion. No extensive stacking is apparent in the solvate crystals.

**Structure.** The most amazing aspect of the $Zr(dsp)_2$ structure at first glance is the obvious dodecahedral geometry of the donor atoms, even though the remainder of the ligand atoms are quite skewed from the two trapezoidal planes spanned by the donor atoms (Table V); cf. Figure 4. These donors fit Orgel's rule[3a] as extended by Clark and co-workers[3b] to $d^0$ $ML_4L'_4$ coordination polyhedra. That is, the N atoms are in the dodecahedral A positions and the O atoms are in the dodecahedral B positions. The latter are π-donor type ligands which can overlap with the empty dπ orbital (the $b_1$ orbital in full $D_{2d}$ symmetry).[16] This perpendicular intersection of ligands is a logical stereochemical arrangement too; however, the extreme skewness of the ligands without an accompanying distortion of the donor atoms shows that the dodecahedral preference at the metal atom is more than just chance.[17] The δ angles (Table VI) and the dodecahedral edge lengths (Table VII) of the $Zr(dsp)_2$ coordination polyhedron suggest that the small distortions which the donor atoms exhibit from an idealized dodecahedron are not along the reaction coordinates toward either a square antiprism or a bicapped-trigonal prism; cf. ref 14c.

The ring distortions from planarity are significant in magnitude and apparently result from the best fit for minimizing ring strain plus molecular packing. The puckering occurs most significantly at the nitrogen atoms with Ph-Ph-NX-CX torsion angles from 24.0 to 29.4° (Table VIII). In the more planar Cu(dsp) thiourea solvate[2c] the analogous torsion angles are apparently less than 5°. Torsion angles of 6.0–14.0° also occur in the rest of the open-chain conjugated backbone in the zirconium chelate, whereas all reported distortions from planarity are less than 7° in the copper chelate.[2c] Even greater nonplanarity is possible; e.g., $dsp^{2-}$ in the $Co^{III}$(dsp)(dbm) chelate,[2b] where $dbm^-$ = dibenzoylmethanato, has a β-cis-type orientation



i.e., one puckered aldimine ring occupies a cis position relative to the remainder of the chelating ligand. Even with the rotations noted in the zirconium chelate, the nitrogen atoms are trigonal planar (within 0.03 Å). Thus the sum of the three angles about the nitrogen atoms are all 360° within experimental error as anticipated for trigonal nitrogen with the fourth valence orbital involved in π bonding. Even in the cobalt(III) chelate,[2b] they are 357–358°, still quite close to planarity.

A consideration of the metal–ligand distances and angles shows no particular surprises. The fairly long Zr–N distances relative to the Zr–O distances, when viewed as numbers, differences, or ratios, are quite typcial for eight-coordinate $d^0$ chelates which have neutral nitrogen donors in the A positions and negatively charged oxygen donors in the B positons as indicated in Table X.

The small $\theta_A$ value (33.4°) is not too surprising given the long Zr–N distances, the ortho nitrogen atoms in each ligand, and the ring to nitrogen interior angles of less than 120°. In fact, the angles are very similar to those observed for $UO_2(dsp)(C_2H_5OH)$,[2a] a seven-coordinate chelate with the same Schiff-base ligand. Other eight-coordinate $d^0$ chelates also

**Table IX.** Spectral Characterization of $Zr(dsp)_2$ and $Zr(sal)_4$

| $Zr(dsp)_2$ | $H_2dsp$ | $Zr(sal)_4$[a] | Hsal | assignment(s) |
|---|---|---|---|---|
| | | Infrared,[b] $cm^{-1}$ | | |
| 1305 | 1270 | 1305 | 1275 | Ph-O str |
| | | 1318 | [1271] | |
| | | [1321] | [1324] | |
| | | [1348] | | |
| 1605 | 1607 | | | C=N str |
| | | 1600 | | C=O str |
| | | 1627 | 1630 | |
| | | [1630] | 1640 | |
| | | | 1650 | |
| | 3400-3450 w | | 3200 vbr | O-H str |
| | | Ultraviolet-Visible,[c] $cm^{-1}$ | | |
| 23 800 sh | | [23 300] | | |
| 27 000 (4.53) | | [26 400 sh] | | |
| | | 27 000 | [28 500] | |
| 29 900 sh | 29 900 (4.28) | 29 300 | 30 300 | |
| 31 300 sh | | | | |
| 33 000 sh | | | | |
| 34 400 (4.61) | | | | |
| | 36 900 (4.37) | 36 500 sh | [37 500] | |
| 39 800 (4.90) | | [38 300] | 38 800 | |
| | | >41 600 | | |
| | | Nuclear Magnetic Resonance, $\tau$[d] | | |
| | −3.0 (1) | | −1.05 s (1) | OH |
| | | | [−1.0] | |
| 1.50 s (1) | 1.34 s (1) | 0.65 s (1) | 0.07 s (1) | aldimine/ aldehyde |
| | | [0.45] | [0.06] | |
| 2.57 s (2) | 2.6 m (2) | | | aromatic (diamine) |
| 2.9 m (2) | | 2.5 m (2) | 2.5 m (2) | aromatic (sal) |
| 3.5 m (1) | 3.1 m (4) | 3.2 m (2) | 3.0 m (2) | |
| 4.0 m (1) | | [2.9 (2), 3.3 (1)] | [3.0 (3)] | |
| | | [6.25 s (3)] | [6.15 s (3)] | $OCH_3$ |
| | | Mass Spectra, *m/e*[e] | | |
| 718 (100) | | 574 (≤0.1) | | parent peak |
| 701 (22) | | 453 (10) | | |
| 612 (22) | | 122 (100) | | |
| 522 (25) | | 121 (75) | | |
| 359 (28) | | | | $(\text{parent peak})^{2+}$ |
| 300 (15) | | 104 (25) | | |
| 224 (12) | | 93 (24) | | |
| 77 (15) | | 76 (30) | | |
| | | 66 (20) | | |
| | | 65 (49) | | |
| | | 53 (13) | | |
| | | 50 (15) | | |
| | | 39 (90) | | |

[a] Analogous values for the 3-methoxy derivative are given in brackets. [b] KBr pellets; w = weak; vbr = very broad. [c] log $\epsilon$ (molar extinction coefficient) in parentheses; $CH_2Cl_2$ solvent; sh = shoulder. [d] $CD_2Cl_2$ solvent; s = singlet; d = doublet; m = multiplet; relative integrated intensities in parentheses. [e] The *m/e* values is followed by relative intensities as measured with a solid-probe inlet heated to 180-220 °C and source temperatures of 225-260 °C; other assignments in Discussion; only the $^{90}Zr$ component is listed for the Zr multiplets.

**Table X.** Bond Length Parameters for Related $d^0$ Chelates[a]

| chelate | M-O | M-N | (M-N) − (M-O) | (M-N)/(M-O) | ref |
|---|---|---|---|---|---|
| $Zr(esam)_4$ | 2.055 | 2.539 | 0.48 | 1.24 | 19 |
| $Zr(q)_4$ | 2.106 | 2.405 | 0.30 | 1.14 | 16a |
| $Zr(dsp)_2$ | 2.097 | 2.428 | 0.33 | 1.15 | this study |
| $Zr(nta)_2$ | 2.130[b]<br>[2.251][c] | 2.439 | 0.31[b]<br>[0.19][c] | 1.15[b]<br>[1.09][c] | 20 |
| $[UO_2(dsp)(C_2H_5OH)]$ | [2.26][d] | [2.545][d] | [0.28][d] | [1.11][d] | 2a |

[a] All distances are average distances in Å; $esam^-$ = *N*-ethylsalicylaldiminato; $nta^{3-}$ = nitrilotriacetato; $q^-$ = 8-quinolinolato. [b] For the O atoms in B positions as above. This is a $ZrN_2O_6$ polyhedron. [c] For the O atoms in A positions. [d] A seven-coordinate complex with all dsp donors in a plane perpendicular to the $UO_2$ axis.

possess $\theta_A$ values [$Zr(esam)_4$, 34.6°;[19] $Zr(nta)_2{}^{2-}$, 34.8°;[20] $Zr(q)_4$, 35.7°[17]] which are lower than the hard-sphere 36.9° value[12] but are closer to the most favorable model value of 35.2°.[12] The $Zr(dsp)_2$ $\theta_B$ value (73.0°) is a little larger than the hard-sphere value (69.5°)[12] but is close to both the most favorable model value (73.5°)[12] and the results for the $Zr(esam)_4$ chelate (73.3°).[19]

The alternating bond lengths of the Schiff-base chelate rings are quite normal; cf. Table XI. Note that skewed rings and donor atoms out of the plane of the other donor atoms [e.g., the second values for the cobalt(III) chelate Co(dsp)(dbm)] do not alter the values appreciably. Also, note that the terminal oxygen–oxygen distances can vary by almost 2 Å without disrupting the other parameters. Thus, the quadridentate Schiff-base is able to chelate with distortions appreciably greater than would be required to go from a dodecahedral to an antiprismatic polytope.

**Spectral Characterization.** The infrared spectral shifts (Table IX) are similar to analogous complexes with other metals. The phenolic C–O stretch is shifted from about 1280

**Table XI.** Ligand Parameters in $H_2dsp$ and $dsp^{2-}$ Chelates[a]

| bond[b] | $Zr(dsp)_2$[c] | $UO_2(dsp)(C_2H_5OH)$[d] | Co(dsp)(dbm)[e] | Cu(dsp)[f] | Co(dsp)[g,h] | $H_2dsp$[g] |
|---|---|---|---|---|---|---|
| | | | Lengths | | | |
| O–C(X1) | 1.318 | $1.34_5$ | 1.297, 1.351 | $1.31_5$ | 1.298 | 1.345 |
| C(X1)–C(X2) | 1.416 | $1.39_5$ | 1.429, 1.406 | | 1.424 | 1.421 |
| C(X2)–C(X) | 1.439 | $1.44_5$ | 1.412, 1.442 | $1.43_5$ | 1.418 | 1.451 |
| C(X)–N | 1.300 | $1.30_5$ | 1.290, 1.284 | 1.29 | 1.317 | 1.288 |
| N–Ph | 1.429 | 1.41 | 1.427, 1.436 | 1.42 | 1.434 | 1.421 |
| Ph–Ph | 1.396 | 1.42 | 1.387 | | 1.390 | |
| O–N bite | 2.723 | $2.75_5$ | 2.796, 2.637 | 2.82 | 2.730 | (2.599) |
| N–N bite | 2.670 | 2.64 | 2.537 | 2.62 | 2.558 | (2.719) |
| O–O | 4.010 | 4.44 | 2.693 | 2.63 | 2.473 | 3.522 |
| | | | Angles | | | |
| OX–CX1–CX2 | 121.3 | 119.7 | 124.2, 123.7 | 124.3 | | |
| CX1–CX2–CX | 122.2 | 124.6 | 123.2, 118.6 | 124.2 | | |
| CX2–CX–NX | 125.6 | 124.0 | 125.5, 121.9 | 125.0 | | |
| CX–NX–Ph | 118.1 | 118.6 | 122.4, 122.0 | 123.2 | 121.0 | 121.0 |
| NX–Ph–Ph | 116.4 | 115.6 | 114.9, 112.1 | 115.9 | | |
| NX–Ph–Ph′ | 123.8 | | 125.8, 125.6 | 123.0 | 125.3 | 125.7<br>120.8[i] |

[a] Bond lengths in Å; angles in degrees. [b] Composites of *A*, *B*, *C*, and *D* parameters listed as X; Ph = phenyl carbons attached to nitrogens, Ph′ = next carbons in phenyl rings; cf. Table VIII. [c] This study; $2.5C_6H_6$ solvate. [d] Reference 2a. [e] Reference 2b; Hdbm = dibenzoylmethane; second value is for "cis" side of ligand. [f] Reference 2c; thiourea solvate; average value for two independent molecules. [g] Reference 2d. [h] Monoclinic cobalt(II) form. [i] Large rotation (52°) about N–Ph on this side.

$cm^{-1}$ to greater than 1300 $cm^{-1}$ in both $Zr(dsp)_2$ and $Zr(sal)_4$, analogous to other chelates of $H_2dsp$[24] and Hsal.[25] The C═N stretch near 1610 $cm^{-1}$ is very similar to that in the free ligand, as has been noted in other chelates containing the $dsp^{2-}$ ligand.[24] The OH stretch of each free ligand disappears upon chelation.

Although the ultraviolet and visible spectra of the chelates were recorded, no interpretations or assignments have been made. The changes in the $Zr(dsp)_2$ spectrum from that of the free ligand are similar to previous observations for Schiff-base chelates of thorium[26] and iron;[27] i.e., additional transitions are evident.

The proton NMR spectra also verify the chelation with shifts of about 0.6 ppm. The retention of a sharp singlet for the aldehydic proton, the shifts in the aromatic protons, and the absence of the phenolic hydroxy ligand resonance in $Zr(sal)_4$ are all consistent with an eight-coordinate chelate. The $Zr(dsp)_2$ aldimine resonance is a sharp singlet shifted upfield from the ligand resonance. The aromatic protons ortho to either the phenolic group or the aldimine group are shifted upfield out of the other aromatic signals and all integrate properly for a symmetric or nonrigid structure.

The mass spectrum of $Zr(dsp)_2$ exhibits a strong parent peak, with a cluster of peaks consistent with the zirconium isotopic abundances. The *m*/*e* 718 base peak corresponds to the monomeric chelate with one zirconium-90 atom, which is most abundant isotope of the element. Other major peaks at *m*/*e* 701, 612, and 522 correspond to loss of $OH^-$, $C_6H_4CH_2O^-$, and $C_6H_5NCHC_6H_4O^-$, respectively. The next strongest peak at *m*/*e* 359 is the doubly charged parent chelate.

The strongest peaks in the $Zr(sal)_4$ spectrum are the charged ligand and fragments thereof, and the strongest peak containing zirconium is the $Zr(sal)_3^+$ peak. The loss of one ligand in the ionization of zirconium chelates has been observed for $Zr(acac)_4$, where the parent peak is only 1% of the $Zr(acac)_3^+$ peak,[28] even though the chelate is eight-coordinate.[29]

Overall, the spectral characterization is consistent with eight-coordination for both the $Zr(dsp)_2$ and $Zr(sal)_4$ chelates. In fact we had communicated[6] this conclusion prior to embarking on the X-ray structure reported herein.

**Acknowledgment.** Analyses were performed by the University of Massachusetts Microanalytical Laboratory. The research was supported through a University of Massachusetts/National Science Foundation Materials Research Laboratory grant. We thank the University of Massachusetts Computer Center for generous allocation of computing time.

**Registry No.** $Zr(dsp)_2 \cdot 2.5C_6H_6$, 70953-88-7; $Zr(sal)_4$, 65531-97-7; $Zr(acac)_4$, 17501-44-9; tetrakis(3-methoxysalicylaldehydato)zirconium(IV), 70891-74-6; 1,2-phenylenediamine, 95-54-5.

**Supplementary Material Available:** Table XII, bond lengths and angles for the benzene solvate molecules; a list of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) Archer, R. D.; Batschelet, W. H.; Illingsworth, M. L. *Org. Coat. Plast. Chem.*, in press.

(2) (a) Bandoli, G.; Clemente, D. A.; Croatto, U.; Vidali, M.; Vigato, P. A. *J. Chem. Soc., Chem. Commun.* **1971**, 1330. (b) Cummins, D.; McKenzie, E. D.; Milburn, H. *J. Chem. Soc., Dalton Trans.* **1976**, 130. (c) Ferrari, M. B.; Fava, G. G.; Pelizzi, C. *Acta Crystallogr., Sect. B* **1976**, *32*, 901. (d) Pahor, N. B.; Calligaris, M.; Delise, P.; Dodic, G.; Nardin, G.; Randaccio. L. *J. Chem. Soc., Dalton Trans.* **1976**, 2478.

(3) (a) Orgel, L. E. *J. Inorg. Nucl. Chem.* **1960**, *14*, 136. (b) Clark, R. J. H.; Lewis, J.; Nyholm, R. S. *J. Chem. Soc.* **1962**, 2460.

(4) Young, R. C.; Arch, A. *Inorg. Synth.* **1946**, *2*, 121.

(5) (a) Pfeiffer, P.; Hesse, T.; Pfitzner, H. *J. Prakt. Chem.* **1937**, *149*, 217. (b) Senier, A.; Shepeard, F. G.; Clarke, R. *J. Chem. Soc.* **1912**, *101*, 1955.

(6) Archer, R. D.; Illingsworth, M. L. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 661.

(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 75.

(8) The function minimized is $\sum w(|F_o| - |F_c|)^2$. Atomic form factors for nonhydrogen atoms were taken from: Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104. Scattering factors for hydrogen atoms were taken from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175. Real and imaginary components of the anomolous dispersion for Zr were taken from: Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(9) Goodness of fit $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, $N_o$ = number of observations = 4485, and $N_v$ = number of variables = 577.

(10) The values in parentheses following the average values are the root-mean-square values of individual esd's and the mean and maximum deviations from the average. Details of the benzene ring structures are available as supplementary material.

(11) The standard Hoard–Silverton[12] nomenclature and appropriate dihedral angles[13,14] are used herein. Refer to the original references for details.

(12) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235.

(13) Lippard, S. J.; Russ, B. J. *Ibid.* **1968**, *7*, 1686.

(14) (a) Porai-Koshits, M. A.; Aslanov, L. A. *J. Struct. Chem.* (*Engl. Transl.*) **1972**, *13*, 244. (b) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. (c) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, *24*, 179.

(15) Merrel, P. H.; Osgood, R. A. *Inorg. Chim. Acta* **1975**, *14*, L33.

(16) Such an A and B position sorting generally occurs for oxygen and nitrogen donors whenever possible; e.g., compare the structure of $Zr(q)_4$[17] with our earlier prediction,[18] where $q^-$ = 8-quinolinolato. The donors of $Zr(esam)_4$[19] and $K_2Zr(nta)_2$[20] also sort in an analogous fashion, although the latter has two of its six oxygen donors in A positions $esam^-$ =

*N*-ethylsalicylaldiminato and nta$^{3-}$ = nitrilotriacetato. However, sulfur and oxygen donors do not sort in this fashion.[21]

(17) Lewis, D. F.; Fay, R. C. *J. Chem. Soc., Chem. Commun.* **1974**, 1046.

(18) Bonds, W. D., Jr.; Archer, R. D.; Hamilton, W. C. *Inorg. Chem.* **1971**, *10*, 1764.

(19) Bradley, D. C.; Hursthouse, M. B.; Rendall, I. F. *J. Chem. Soc., Chem. Commun.* **1970**, 368.

(20) Hoard, J. L.; Willstadter, E.; Silverton, J. V. *J. Am. Chem. Soc.* **1965**, *87*, 1610.

(21) (a) Steffen, W. L.; Hawthorne, S. L.; Fay, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 6757. (b) Hawthorne, S. L.; Bruder, A. H.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2114. (c) Steffen, W. L.; Fay, R. C. *Ibid.* **1978**, *17*, 2120.

(22) The structural characterization of an analogous d$^2$ species [e.g., W(dsp)$_2$] would be particularly enlightening because the positions of the N and O donors in the dodecahedron should be reversed. Thus, the ligand would no longer span *m* and *a* edges. Instead, the reversal would cause an alternate wrapping such as *gbg*, which allows the ligands to wrap without severe distortions from planarity and with the N and O donors in the appropriate positions.[23] The two chelate ring *b* edges for this isomer would need to be somewhat shortened, which might lead to another isomer with less ligand planarity instead.

(23) Donahue, C. J. Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1977.

(24) (a) Bellamy, L. J.; Branch, R. F. *J. Chem. Soc.* **1954**, 4491. (b) Marvel, C. S.; Aspey, S. A.; Dudley, E. A. *J. Am. Chem. Soc.* **1956**, *78*, 4905. (c) Mehrotra, R. C.; Gupta, V. D.; Bharara, P. C. *Indian J. Chem.* **1973**, *11*, 814. (d) Biradar, N. S.; Goudar, T. R.; Mahale, V. B.; Kulkarni, V. H. *J. Karnatak Univ.* **1973**, *18*, 19.

(25) Percy, G. C.; Thornton, D. A., *J. Inorg. Nucl. Chem.* **1973**, *35*, 2719.

(26) Biradar, N. S.; Kulkarni, V. H., *Z. Anorg. Allg. Chem.* **1972**, *387*, 275.

(27) Bertrand, J. A.; Eller, P. G. *Inorg. Chem.* **1974**, *13*, 927.

(28) Tsuge, S.; Leary, J. J.; Isenhour, T. L. *Anal. Chem.* **1973**, *45*, 198.

(29) Silverton, J. V.; Hoard, J. L. *Inorg. Chem.* **1963**, *2*, 243.

# Notes

Contribution from the Departments of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, and The University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

## Synthesis and Structure of 1-Methyl-1,3,5,7-tetraazaadamantan-1-ium Octaiodide, $[(CH_2)_6N_4CH_3]_2I_8$. A New Outstretched *Z* Configuration for the Polyiodide Ion $I_8^{2-}$

P. K. Hon, Thomas C. W. Mak, and James Trotter*

*Received April 25, 1979*

Among members of the halogen family, iodine exhibits the highest tendency for catenation, giving rise to a variety of polyiodide species of the general formula $I_x^{n-}$.[1] These anion complexes, which can be either discrete or polymeric, crystallize with large counterions such as $Cs^+$, $R_4N^+$, and protonated organic nitrogen compounds. Values of *x* ranging from 3 to 16 are known, with $n = 1$ for *x* odd and $n = 2$ or 4 for *x* even. While a rather large number of triiodides has been extensively investigated,[1,2] relatively little is known about the higher polyiodides, and the bulk of our knowledge about these systems is derived from X-ray crystallographic studies. The only well-established discrete higher polyiodide entities are $I_4^{2-}$,[3,4] $I_5^-$,[5,6] $I_8^{2-}$,[7] $I_9^-$,[8] and $I_{16}^{4-}$[9] (Table I). Other higher polyiodides, such as (phenacetinH)$I_5$,[10] (quinuclidineH)$I_5$,[11] $[(C_2H_5)_4N]I_7$,[12] and $[(\text{pyridine})_2I]I_7$,[13] adopt infinite network structures in which no separate polyiodide aggregates can be distinguished.

Recently we prepared[14] and determined the crystal and molecular structure[15] of hexamethylenetetramine oxide (1,3,5,7-tetraazaadamantane *N*-oxide), $(CH_2)_6N_4O$. In an attempt to prepare donor–acceptor complexes from the system $(CH_2)_6N_4O$–$I_2$–$CHCl_3$, we unexpectedly isolated the title compound as one of the products. Structural characterization of this new polyiodide, as reported in the present paper, revealed an outstretched form of the $I_8^{2-}$ anion differing from the *Z* configuration observed in its cesium salt[7] (Figure 1).

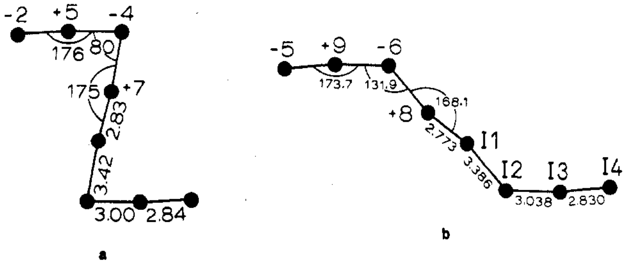


**Figure 1.** Dimensions of the $I_8^{2-}$ ion in (a) $Cs_2I_8$ and (b) $[(CH_2)_6N_4CH_3]_2I_8$. The signed figures represent deviations (in Å × $10^{-2}$) of atoms from an exactly planar configuration.

### Experimental Section

Hexamethylenetetramine oxide, $(CH_2)_6N_4O$, was prepared by the reaction of hexamethylenetetramine with 30% aqueous hydrogen peroxide and recrystallized from chloroform.[14] The title compound was obtained by slow evaporation of a chloroform solution of $(CH_2)_6N_4O$ ($1.95 \times 10^{-3}$ M) and $I_2$ ($3.53 \times 10^{-3}$–$5.30 \times 10^{-3}$ M) in air at ambient temperatures. A small crop of black crystals with dark metallic luster was deposited after several days. When carbon tetrachloride was used to wash the crystals, a reddish violet color appeared in the resultant liquid. After the product had been stored in a clear plastic vial for a few hours, reddish violet stains appeared on the inside wall. These observations indicate that some $I_2$ molecules adhere loosely to the surface of freshly prepared crystals. Anal. Calcd for $[(CH_2)_6N_4CH_3]_2I_8$: C, 12.68; H, 2.28; N, 8.45. Found: C, 12.81; H, 2.22; N, 8.55. Upon heating, the black crystals changed irreversibly into a light orange color at about 127 °C and eventually melted at 160 °C. A better yield of the compound was obtained by reacting equivalent quantities of $(CH_2)_6N_4$ and $CH_3I$ and an excess of $I_2$ in chloroform. However, two other kinds of relatively unstable orange and reddish brown crystals appeared in the same preparation. These side products were suspected to be $(CH_2)_6N_4 \cdot I_2$[16] and $(CH_2)_6N_4 \cdot 2I_2$[16] and were manually separated from the black crystals of $[(CH_2)_6N_4CH_3]_2I_8$.

A crystal in the shape of a polyhedron with cross sections of 0.2–0.45 mm was selected. Preliminary precession photographs and accurate measurements on a Nonius CAD-4 diffractometer with graphite monochromator and Mo K$\alpha$ radiation ($\lambda$ 0.71069 Å) indicated space group $P2_1/c$ and the following cell parameters: $a = 11.258$ (2) Å, $b = 9.827$ (1) Å, $c = 14.150$ (3) Å, $\beta = 92.08$ (1)°, and $V = 1564.4$ Å$^3$. For $Z = 2$ and a molecular weight of 1325.74, the calculated density is 2.814 g cm$^{-3}$, in reasonable agreement with the measured density of 2.79 (2) g cm$^{-3}$ by flotation in carbon tetrachloride/1,1,2,2-tetrabromoethane.

Intensities for 4540 unique reflections with $\theta < 30°$ were collected by using the $\omega$-scan technique, and three standard reflections were measured every hour to check the stability of the crystal and the electronics. Data were corrected for absorption ($\mu = 80.4$ cm$^{-1}$) by the Gaussian integration method,[17,18] and transmission factors ranged from 0.031 to 0.151. Of the complete data set, 2736 independent reflections (60.3%) had intensities greater than $3\sigma(I)$ above background.

The structure was solved by direct methods, and all 15 nonhydrogen atoms in the asymmetric unit were refined anisotropically by full-matrix least-squares techniques. In the last cycle all 12 methylene H atoms were introduced and assigned the same isotropic temperature factor $B = 5.0$ Å$^2$, yielding a conventional discrepancy index $R \equiv \sum||F_o| - |F_c|| / \sum|F_o| = 0.096$. The final difference map did not reveal

---

*To whom correspondence should be addressed at The University of British Columbia.