acting with pyrazine, with a value of the rate constant that is of the same order in both cases, thus reflecting a minor effect of the auxiliary ligands (NH_3 vs. CN^-) on the substitutional reactivity of the Ru–OH_2 bond.[11,49]

Conclusions

The iron and ruthenium pentacyanonitrosyl salts of sodium constitute a unique pair of substances where the comparative π-donor capabilities of both metal centers can be successfully assessed; this is favored by the analogous environment around the metals, as well as by the dominant character of the M(II)(d_{xz},d_{yz})–π^*(NO) interaction in the overall bonding scheme, the $\sigma(NO^+)$ contribution remaining negligible or at least essentially constant.

The consequences of the higher π-donor ability of Ru are reflected in the changes found in all of the measured fundamental vibrations in both complexes, including even the O–H stretchings of weakly hydrogen-bonded water molecules. The energy of electronic transitions are also strongly influenced by this phenomenon.

The most significant structural result that can be reasonably ascribed to the same origin is the relative shortening of the trans-C–N distance, a feature that could not be put in evidence in [FeNO]. A similar line of reasoning explains the equality of cis- and trans-Ru–C distances, as a result of self-compensating contributions. Thus, the cyanonitrosylruthenium complex behaves differently compared to $RuCl_5NO^{2-}$, as expected from the bonding properties of the ligands involved.

The competition of cyanide for the π-electron density also places [RuNO] in one of the extremes of a series of related $\{RuNO\}^6$ complexes, thus showing a tendency for weaker Ru–N bonds (higher Ru–N distance and lower ν(Ru–N)) and stronger N–O bonds (lower N–O distance[51] and higher ν(NO)).[3,18]

Finally, although the general reactivity picture is indeed common to both [RuNO] and [FeNO], a direct correlation between ν(NO) and electrophilic reactivity toward OH^- seems not to be operative in a strictly quantitative way; more detailed work will be performed in order to assess the influence of other possible factors, as well as to expand the studies to other nucleophiles. On the other hand, several evidences point to the common final product of these addition reactions to be $Ru(CN)_5H_2O^{3-}$, a result that allows for fruitful developments in the comparative chemistry of Ru(II) complexes.

Acknowledgment. This work was, in part, supported by the Comisiõn de Investigaciones Cientificas (Prov. Buenos Aires) and Secretaria de Ciencia y Tẽcnica. Valuable comments from Prof. E. Diemann (University of Bielefeld) are also gratefully acknowledged.

Registry No. $Na_2Ru(CN)_5NO{\cdot}2H_2O$, 92763-38-7; $Ru(CN)_5NO_2$, 40209-40-3; $Ru(CN)_5H_2O^{3-}$, 74009-27-1; OH^-, 14280-30-9; SH^-, 15035-72-0; SO_3^{2-}, 14265-45-3; ammonia, 7664-41-7; hydrazine, 302-01-2.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters, positional and equivalent isotropic thermal parameters, and interatomic distances and bond angles within sodium polyhedra and a stereoscopic projection down *c* showing the packing of the structure (30 pages). Ordering information is given on any current masthead page.

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(51) However, comparisons between N–O and Ru–N distances for structurally related complexes should be made with caution, as changes are evidently of the order of experimental errors (cf. the strikingly low number found for the N–O distance in $RuCl_5NO^{2-}$, 1.112 (7) Å).[9]

Contribution from the Department of Chemistry,
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Syntheses and Molecular Structures of Related Six- and Eight-Coordinate Complexes: Tetrachloro(2,2′-bi-2-thiazine)zirconium(IV), Tetrachlorobis(2,2′-bi-2-thiazoline)zirconium(IV), and Bis(2,2′-bi-2-thiazoline)tetrakis(isothiocyanato)zirconium(IV)

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Received February 22, 1984

The crystal and molecular structures of the six-coordinate complex $ZrCl_4(C_8H_{12}N_2S_2)$ (**1**) and the eight-coordinate complexes $ZrCl_4(C_6H_8N_2S_2)_2{\cdot}2CH_3CN$ (**2**) and $Zr(NCS)_4(C_6H_8N_2S_2)_2$ (**3**) have been determined from single-crystal X-ray diffraction data collected by the θ–2θ scan technique. Compound **1** crystal data: $P2_1/n$, a = 18.478 (4) Å, b = 10.930 (3) Å c = 16.656 (4) Å, β = 109.76 (2)°, Z = 8, ρ_{calcd} = 1.82 g/cm^3, ρ_{obsd} = 1.80 g/cm^3. Compound **2** crystal data: $C2/c$, a = 14.199 (8) Å, b = 14.933 (7) Å, c = 13.825 (7) Å, β = 112.34 (4)°, Z = 4, ρ_{calcd} = 1.62 g/cm^3, ρ_{obsd} = 1.62 g/cm^3. Compound **3** crystal data: $P2_1/c$, a = 15.161 (8) Å, b = 21.627 (8) Å, c = 16.350 (3) Å, β = 96.99 (3)°, Z = 8, ρ_{calcd} = 1.67 g/cm^3, ρ_{obsd} = 1.68 g/cm^3. All three structures were refined by full-matrix least squares to the residuals 0.069, 0.053, and 0.053, respectively. Comparison of the three structures reveals a great deal about the factors that influence the shape of the coordination polyhedron. The two bithiazoline complexes, **2** and **3**, have geometries intermediate between an ideal dodecahedron and an ideal square anitprism. The bithiazine ligand is too large to permit the formation of an eight-coordinate $ZrCl_4(L\text{–}L)_2$ complex; thus, compound **1** results. The Zr–N bond lengths follow the crowding effects with 2.300 (10) Å for **1**, 2.463 (10) Å for **2**, and 2.388 (15) Å for **3**.

Introduction

The monomeric complexes tetrachloro(2,2′-bi-2-thiazine)zirconium(IV), $ZrCl_4(C_8H_{14}N_2S_2)$, tetrachlorobis(2,2′bi-2-thiazoline)zirconium(IV), $ZrCl_4(C_6H_8N_2S_2)_2$, and bis(2,2′-bi-2-thiazoline)tetrakis(isothiocyanato)zirconium(IV), $Zr(NCS)_4(C_6H_8N_2S_2)_2$, have been prepared as part of a study of the coordination of 2,2′-bi-2-thiazine (btz) and 2,2′-bi-2-thiazoline (bt) in related complexes. Previous use of these heterocyclic dimers as ligands has established that they normally coordinate through the nitrogen atoms.[1-3] Few complexes have been synthesized with either ligand, and no single-crystal structural studies have been reported on any com-

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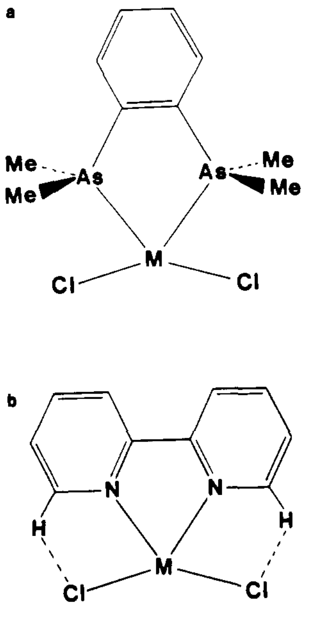
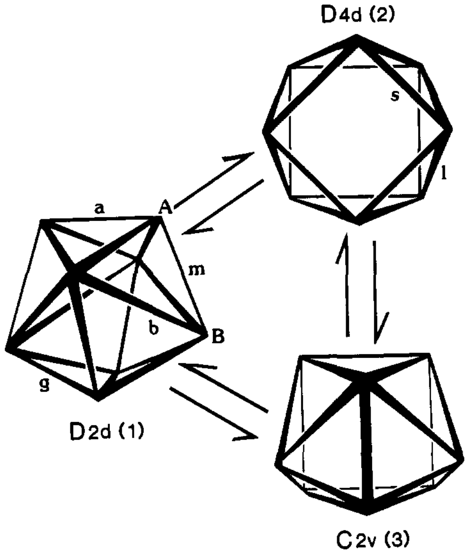


Figure 1. (a) Diagram of dodecahedral trapezoidal plane in $MCl_4(diars)_2$. (b) Theoretical dodecahedral trapezoidal plane for $MCl_4(bpy)_2$.

plexes involving these ligands or of the ligands alone. Our interest in these ligands arises because they provide a means to examine the stereochemical interactions associated with the coordination of bulky monodentate and bidentate ligands on early transition-metal ions. In the case of $M(L-L)_2X_4$ complexes, four halide ligands (e.g., Cl, Br) are sufficiently large so that X–M–X angles >90° are sterically required. Thus, the preferred conformation is a dodecahedron[4] (**1**), with the bidentate ligands spanning the adjacent A sites and the halide atoms occupying the B sites. This dodecahedral arrangement places constraints on the shape of the bidentate ligands in order to avoid steric interference with the halide atoms. Previous structural studies of $M(L-L)_2X_4$ complexes have been of compounds where either there is little possibility of steric interference by the bidentate ligands or the halide atoms were small. Examples of the first case are the $M(diars)_2X_4$ (X = Cl, Br) complexes,[5-9] which all have dodecahedral coordination polyhedra with the ligands in the expected arrangement. The diars ligand has a very small normalized bite, 1.19, and fits comfortably on the *a* edge of the dodecahedron and the substitutents (Me, Et) on the As atoms fall on both sides of the halide atoms positioned on the B sites (Figure 1a) with little net steric interference.[10-16] In the second case, either the small halide atoms are positioned to avoid steric interference with a large bidentate ligand (Figure 1b), resulting in a distinctly nondodecahedral coordination polyhedron, or else a lower coordination number geometry results. For example, the rigidly planar bidentate ligand 2,2′-bipyridine (bpy) only forms six-coordinate $M(bpy)X_4$ complexes where X = Cl,[17,18] and the only eight-coordinate complex known is $Zr(bpy)_2F_4$.[19] No structure is known for this compound, but two pseudohalide analogues show the likely distortion. The steric interactions between the NCS and bpy ligands in $Nb(NCS)_4(bpy)_2$ and $Zr(NCS)_4(bpy)_2$ strongly distort the expected dodecahedra to almost perfect square antiprisms (**2**),[20] with the bidentate ligands spanning two opposite *l* edges.

In this paper we have examined the structures of three compounds for the consequences of the steric interactions between the two different intermediate sized bidentate ligands, btz and bt, and two different halide ligands, Cl and NCS, and also provide the first structural descriptions for these bidentate ligands.



Experimental Section

In order to prevent hydrolysis, the starting materials and products were handled and stored under an inert atmosphere and the reactions were conducted in previoulsy evacuated vessels.

Materials. The ligands, 2,2′-bi-2-thiazine and 2,2′-bi-2-thiazoline, were prepared by using the methods described by Tomalia and Paige.[21] The compounds were further purified by extraction and subsequent crystallization as suggested by Nelson et al.[3] These products were dried in vacuo prior to use. Zirconium tetrachloride, obtained from Research Organic/Inorganic Chemical Corp. was sublimed in an evacuated tube at 240 °C. Analytical grade 1,2-dichloroethane, acetonitrile, and toluene were dried and outgassed over P_2O_5 and stored over Linde type 4A molecular sieves.

Preparation and Characterization. $ZrCl_4(C_8H_{12}N_2S_2)$. Approximately 50 mL of 1,2-dichloroethane was vacuum distilled onto a mixture of 0.60 g of btz (3.0 mmol) and 0.69 g of $ZrCl_4$ (3.0 mmol). After 5 h of stirring, the white precipitate that had formed was filtered and dried in vacuo. Anal. Calcd for $ZrCl_4(C_8H_{12}N_2)$: C, 22.19; H, 2.79; N, 6.47; Cl, 32.75. Found: C, 21.82; H, 2.83; N, 6.53; Cl, 32.57. The infrared spectrum was taken as a Nujol mull and showed the following absorptions: 1561 s, 1545 w, 1366 w, 1287 m, 1202 w, 1167 m, 1156 m, 1105 m, 1070 w, 1032 w, 990 w, 873, 765 s, 692 w, 483 w, 440 m, 333 s, 311 s, 250 w cm^{-1}.

Clear, colorless crystals suitable for X-ray work were formed by slowly cooling a solution of the complex in a 50/50 mixture of toluene and acetonitrile. After the supernatant solution was decanted, the

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Table I. Summary of Crystallographic Data and Data Collection Parameters for $ZrCl_4(btz)$, $ZrCl_4(bt)_2 \cdot 2CH_3CN$, and $Zr(NCS)_4(bt)_2$

parameter	$ZrCl_4(btz)$	$ZrCl_4(bt)_2 \cdot 2CH_3CN$	$Zr(NCS)_4(bt)_2$
space group	$P2_1/n$	$C2/c$	$P2_1/c$
a, Å	18.478 (4)	14.199 (8)	15.161 (8)
b, Å	10.930 (3)	14.933 (7)	21.627 (8)
c, Å	16.656 (4)	13.825 (7)	16.350 (3)
β, deg	109.76 (2)	112.34 (4)	96.99 (3)
V, Å^3	3166 (1)	2711 (3)	5321 (4)
ρ_{calcd}, g cm^{-3}	1.82	1.62	1.67
ρ_{obsd},^{a} g cm^{-3}	1.80	1.62	1.68
Z	8	4	8
cryst size, mm	0.18 × 0.10 × 0.05	0.38 × 0.29 × 0.31	0.43 × 0.32 × 0.23
μ(Mo Kα), cm^{-1}	13.6	16.3	10.3
$2\theta_{min}$–$2\theta_{max}$, deg	4–50	4–60	4–55
no. of unique data	6573	3641	10417
no. of data used	3072	3534	6456
P^b	0.0072	0.0040	0.0036
no. of variables	307	165	595
R	0.069	0.053	0.053
R_w	0.030	0.034	0.035
ρ_{max}, e/Å^3	0.7	0.4	1.0
$\Delta:\sigma^c$	0.03	0.05	0.05

^{a} Measured by flotation. ^{b} Instrument instability constant. ^{c} Largest shift (Δ) to error (σ) ratio in the final least-squares cycle.

crystals were washed with pentane and dried in vacuo.

$ZrCl_4(C_6H_8N_2S_2)_2$. Approximately 50 mL of acetonitrile was vacuum distilled onto a mixture of 0.5 g of bt (2.9 mmol) and 0.34 g of $ZrCl_4$ (1.5 mmol). After the mixture was stirred for several hours, the white precipitate that had formed was filtered and dried in vacuo. Anal. Calcd for $ZrCl_4(C_6H_8N_2S_2)_2$: C, 24.95; H, 2.79; N, 9.70. Found: C, 24.99; H, 2.54; N, 9.90. The infrared spectrum was taken as a Nujol mull and showed the following absorption: 1562 w, 1586 s, 1433 m, 1371 w, 1341 w, 1245 s, 1200 w, 1158 w, 1072 s, 1058 m, 1008 s, 969 s, 947 m, 939 m, 921 m, 888 w, 843 w, 750 w, 690 w, 572 m, 488 m, 378 w, 300 s, 273 w, 218 m cm^{-1}.

Clear, colorless crystals suitable for X-ray work were obtained by slowly cooling a solution of the complex in a 40/60 toluene/acetonitrile mixture. After the supernatant solution was decanted, the crystals were washed with pentane and dried under flowing dry nitrogen. The crystals became opaque and lost structural integrity if subjected to vacuum, indicating the possible inclusion of solvent in the crystal structure. This was borne out by the subsequent structural analysis.

$Zr(NCS)_4(C_6H_8N_2S_2)_2$. Approximately 25 mL of acetonitrile was combined with a mixture of 0.30 g of $ZrCl_4$ (1.28 mmol) and 0.50 g of KNCS (5.15 mmol) under an inert atmosphere. After the mixture was stirred for 3 h, the KCl precipitate was filtered with a medium frit and washed with a small amount (3 mL) of dry acetonitrile. The combined solutions were added to a solution of 0.44 g of bt (2.55 mmol) in 25 mL of toluene. After the mixture was stirred for 5 h, the small amount of precipitate formed was filtered away. The resulting solution was concentrated by evaporation and then cooled slowly. Large crystals suitable for X-ray work formed in a few days. After the supernatant solution was decanted, the crystals were washed with pentane and dried in vacuo. Anal. Calcd for $Zr(NCS)_4(C_6H_8N_2S_2)_2$: C, 28.76; H, 2.41; N, 16.78. Found: C, 29.04; H, 2.33; N, 16.89.

X-ray Data Collection. Crystals of the tetrachloro compounds became opaque and lost structural integrity after exposure to the atmosphere; hence, these crystals were placed in carefully dried glass capillary tubes that were then sealed. Although the thiocyanate complex was apparently unaffected by exposure to air, it was handled in the same way. Preliminary precession photographs indicated that all three crystals are monoclinic. The systematic extinctions observed in these photographs indicated the space groups given in Table I; in the case of $ZrCl_4(bt)_2$ the centrosymmetric choice of $C2/c$ was made and confirmed by the successful structure analysis. Other crystallographic data are also given in this table along with a summary of the data collections and structure refinements. In all cases the lattice parameters were obtained by a least-squares fit to the setting angles for 15 reflections from each crystal performed on a Syntex P$\bar{1}$ autodiffractometer. The collection and preliminary data analysis was completed by using methods described by Post et al.[22] Analytical absorption corrections[23,24] were applied with the linear absorption coefficients listed in the table. The periodic monitoring of four reflections was used to correct for slight (1–3%) intensity variations during the collections and to establish the instrument instability factors shown in the table. In all three cases examination of ω scans for selected reflections showed that the crystals were single and of good quality.

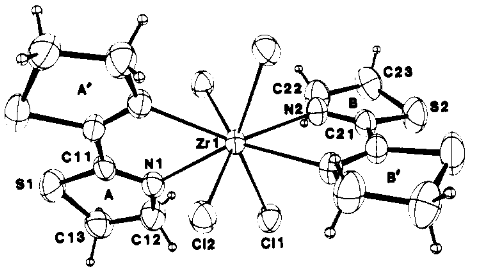

Figure 2. Perspective drawing of the $ZrCl_4(bt)_2$ molecule.

Structure Solution. Examination of a Patterson synthesis[25] for $ZrCl_4(btz)$ failed to provide the positions of the two Zr atoms in the asymmetric unit. Therefore, the MULTAN system of computer programs[26-28] was employed. It was necessary to reduce the symmetry to $P2_1$ before a usable set of Zr atom positions could be found. The remaining atoms were found from a series of difference syntheses in the proper space group, $P2_1/n$. In the case of $ZrCl_4(bt)_2 \cdot 2CH_3CN$, the Patterson synthesis indicated that the Zr atom is positioned on the crystallographic twofold axis in the space grop $C2/c$ and also indicated the positions of the two independent Cl atoms. Difference syntheses revealed the remaining atoms. For $Zr(NCS)_4(bt)_2$, the Patterson synthesis could be interpreted to derive the positions of the two independent Zr atoms, and subsequent difference syntheses revealed the remaining atoms.

Structure Refinement. All three structure refinements proceeded in approximately the same way; all used neutral-atom scattering factors and included the anomalous corrections for Zr and Cl.[29] For $ZrCl_4(btz)$ and $Zr(NCS)_4(bt)_2$ the hydrogen atoms were placed at idealized positions on their respective C atoms with fixed isotropic temperature factors (U = 0.05 Å^2). These positions also coincided with peaks in the respective difference syntheses calculated after a refinement of anisotropic thermal parameters for the non-hydrogen atoms. For $ZrCl_4(bt)_2 \cdot 2CH_3CN$, the hydrogen atoms were placed according to positions of peaks (0.5–0.6 e/Å^3) found in a difference synthesis and were assigned a fixed temperature factor (U = 0.055 Å^2). Those on the acetonitrile molecule were given a larger temperature factor (U = 0.093 Å^2) appropriate for the motion of this group.

Large-block least squares was employed for the final refinements of the two larger structures. There were 307 parameters in three blocks for $ZrCl_4(btz)$ and 595 parameters in seven blocks for $Zr(NCS)_4(bt)_2$; the hydrogen atom positions were not refined. The final refinement for $ZrCl_4(bt)_2 \cdot 2CH_3CN$ used a full matrix of 165 parameters and included the hydrogen atom positions. The numerical details of these last refinements are given in Table I, and listings of the anisotropic thermal parameters, calculated hydrogen atom positions, and final values of $|F_o|$, $|F_c|$, and phases for all reflections are available as supplementary material.

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Table II. Fractional Coordinates[a] ($\times 10^4$) and Equivalent Thermal Parameters[b] ($\times 10^3$) for $ZrCl_4(btz)$

atom	*x*	*y*	*z*	U_{eq}
Zr(1)	1688.6 (5)	1820.2 (9)	883.9 (6)	46.8
Cl(11)	467 (1)	1915 (2)	1133 (2)	61
Cl(12)	1712 (2)	−355 (2)	901 (2)	75
Cl(13)	2771 (2)	2059 (3)	435 (2)	79
Cl(14)	2380 (2)	2359 (3)	2318 (2)	96
S(11)	−195 (2)	3216 (3)	−1730 (2)	70
S(12)	660 (2)	5404 (3)	−816 (2)	78
N(11)	901 (4)	1894 (7)	−514 (4)	44
N(12)	1446 (4)	3813 (6)	428 (5)	46
C(11)	575 (5)	2912 (9)	−827 (6)	39
C(12)	622 (6)	766 (9)	−995 (7)	66
C(13)	205 (7)	914 (9)	−1958 (7)	51
C(14)	−475 (6)	1726 (12)	−2153 (6)	66
C(15)	954 (6)	4028 (8)	−309 (6)	44
C(16)	1868 (6)	4824 (10)	960 (7)	68
C(17)	1968 (6)	5932 (10)	464 (7)	63
C(18)	1258 (7)	6485 (9)	−81 (7)	68
Zr(2)	6506.5 (5)	1599.1 (8)	1440.6 (5)	38.8
Cl(21)	7786 (1)	1506 (3)	1371 (2)	66
Cl(22)	6338 (2)	−550 (2)	1482 (2)	65
Cl(23)	5162 (1)	2050 (2)	1200 (1)	50
Cl(24)	6894 (1)	2107 (2)	2915 (1)	55
S(21)	6039 (2)	5249 (2)	−306 (2)	51
S(22)	5762 (2)	3064 (3)	−1474 (2)	59
N(21)	6493 (4)	3602 (6)	986 (4)	39
N(22)	6141 (4)	1701 (7)	−17 (4)	39
C(21)	6220 (5)	3833 (3)	188 (6)	38
C(22)	6716 (5)	4614 (9)	1607 (6)	48
C(23)	6156 (5)	5681 (9)	1366 (6)	48
C(24)	6167 (5)	6284 (8)	578 (6)	52
C(25)	6051 (5)	2743 (9)	−390 (6)	36
C(26)	6030 (6)	572 (8)	−509 (6)	49
C(27)	6082 (7)	631 (10)	−1374 (7)	63
C(28)	5593 (6)	1547 (11)	−1922 (6)	66

[a] Value in parentheses in this and all subsequent tables is the estimated standard deviation in the last significant figure of the value shown. [b] Calculated from $U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_1, U_2, and U_3 are the principal mean-square radii of the thermal ellipsoid.

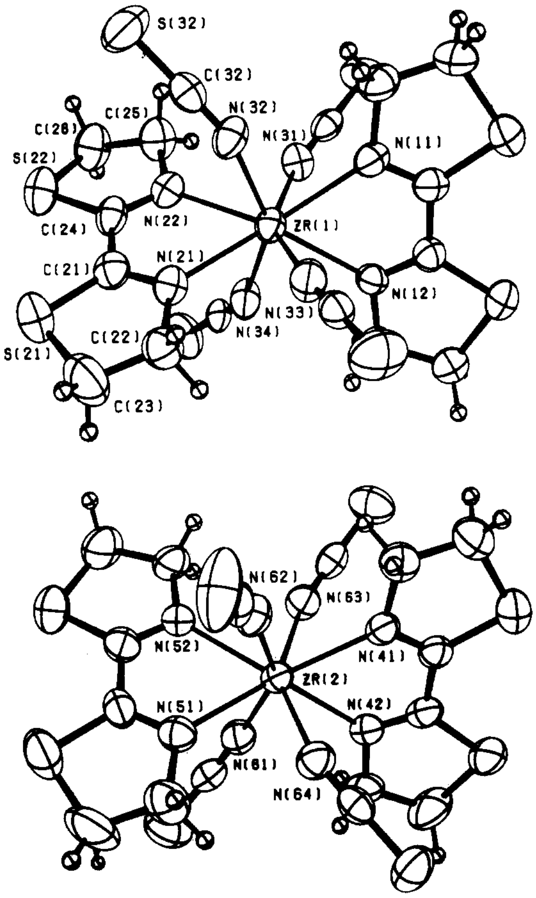

Figure 3. Perspective drawings of the $Zr(NCS)_4(bt)_2$ molecules.

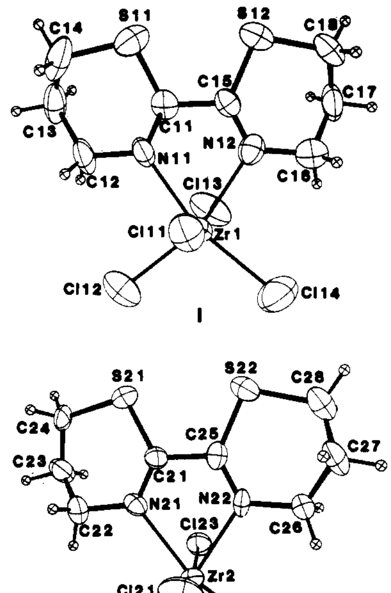

Figure 4. Perspective drawings of the $ZrCl_4(btz)$ molecules.

Results and Discussion

Final atomic coordinates and the equivalent thermal parameters for the non-hydrogen atoms in $ZrCl_4(btz)$, $Zr(NCS)_4(bt)_2$, and $ZrCl_4(bt)_2{\cdot}2CH_3CN$ are given in Tables II–IV, respectively, along with the estimated standard deviations derived from the least-squares analyses. Atomic coordinates with standard deviations for the hydrogen atoms in $ZrCl_4(bt)_2{\cdot}2CH_3CN$ are given in Table V. Figures 2–4 show perspective views of $ZrCl_4(bt)_2$, $Zr(NCS)_4(bt)_2$, and $ZrCl_4(btz)$, respectively, with each atom represented as an ellipsoid consistent with the thermal parameters.

The eight-coordinate $ZrCl_4(bt)_2$ is a monomeric complex situated on a crystallographic twofold axis that passes through both bt ligands so that the asymmetric unit contains Zr, two half-bt ligands, and two Cl atoms. One CH_3CN molecule is also part of the asymmetric unit. Selected interatomic distances within the coordination polyhedron are given in Table VI. Both independent molecules in $Zr(NCS)_2(bt)_2$ are also eight-coordinate monomeric complexes; selected interatomic distances within these coordination polyhedra are given in Table VII. The two independent molecules of $ZrCl_4(btz)$ are six-coordinate, and selected interactomic distances within the coordination polyhedra are given in Table VIII. The bond distances and angles for the polyatomic ligands NCS, bithiazoline, and bithiazine are given in Tables IX–XII. Analysis of this data indicates that the best description of the eight-coordinate polyhedra for the first two compounds is a distorted dodecahedron (**1**),[4] with the bt ligands spanning the *a* edges and the halide ligands occupying the B sites. A least-squares fitting[30] of the normalized atom positions for $ZrCl_4(bt)_2$ to an ideal D_{2d} dodecahedron gave a smaller root-mean-square separation, 0.080, between the atoms and the ideal positions than for the best square antiprism (**2**), 0.124. Similar values were obtained for the normalized atom positions for the two molecules in $Zr(NCS)_4(bt)_2$. The molecule around

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Table III. Fractional Coordinates ($\times 10^4$) and Equivalent Thermal Parameters ($\times 10^3$) for $Zr(NCS)_4(bt)_2$

atom	*x*	*y*	*z*	U_{eq}
Zr(1)	4258.9 (4)	506.2 (2)	2474.6 (3)	43
N(11)	3926 (3)	1575 (2)	2698 (3)	47
N(12)	5476 (3)	1062 (2)	3174 (3)	43
N(21)	3838 (3)	−514 (2)	2838 (3)	50
N(22)	3878 (3)	−155 (2)	1297 (3)	47
N(31)	4592 (3)	1038 (2)	1440 (3)	52
N(32)	2828 (3)	591 (2)	2124 (3)	52
N(33)	4030 (3)	545 (2)	3766 (3)	57
N(34)	5425 (3)	−55 (2)	2375 (3)	55
S(11)	4367.1 (12)	2705.0 (7)	3163.1 (11)	67
S(12)	6198.3 (11)	1987.8 (8)	4038.9 (10)	63
S(21)	3374.8 (12)	−1662.3 (8)	2516.4 (12)	72
S(22)	3332.2 (12)	−1991.7 (8)	580.7 (11)	70
S(31)	4800.6 (13)	2078.7 (9)	501.6 (12)	83
S(32)	1335.5 (12)	289.3 (9)	1064.0 (12)	80
S(33)	3752.3 (13)	715.2 (9)	5397.9 (11)	79
S(34)	6455.5 (13)	−831.3 (8)	1533.7 (12)	79
C(11)	4536 (4)	1924 (3)	3071 (3)	45
C(12)	3152 (4)	1946 (3)	2361 (4)	57
C(13)	3315 (4)	2626 (3)	2543 (4)	75
C(14)	5374 (4)	1620 (3)	3396 (3)	46
C(15)	6358 (4)	819 (3)	3521 (4)	65
C(16)	6874 (4)	1299 (3)	4062 (4)	62
C(21)	3625 (4)	−912 (3)	2272 (4)	50
C(22)	3822 (4)	−801 (3)	3652 (4)	62
C(23)	3663 (5)	−1484 (3)	3579 (4)	88
C(24)	3626 (4)	−710 (3)	1416 (4)	48
C(25)	3791 (4)	−13 (3)	419 (4)	61
C(26)	3722 (4)	−612 (3)	−74 (4)	69
C(31)	4680 (4)	1475 (3)	1048 (3)	44
C(32)	2206 (4)	469 (3)	1691 (3)	44
C(33)	3915 (4)	621 (2)	4450 (4)	48
C(34)	5860 (4)	−383 (3)	2028 (4)	46
Zr(2)	−42.4 (4)	1641.0 (2)	3206.6 (3)	41
N(41)	−824 (3)	711 (2)	3393 (3)	45
N(42)	−470 (3)	1107 (2)	1949 (3)	45
N(51)	−104 (3)	2726 (2)	3418 (3)	52
N(52)	1255 (3)	2033 (2)	4032 (3)	49
N(61)	684 (3)	2082 (2)	2296 (3)	55
N(62)	−449 (3)	1709 (2)	4425 (3)	54
N(63)	907 (3)	888 (2)	3363 (3)	54
N(64)	−1400 (3)	1911 (2)	2738 (3)	55
S(41)	−1527.7 (13)	−352.8 (8)	2907.0 (11)	77
S(42)	−1402.8 (13)	288.1 (8)	1041.2 (10)	68
S(51)	565.0 (15)	3794.7 (8)	3904.8 (13)	85
S(52)	2266.1 (14)	2926.6 (9)	4691.2 (13)	37
S(61)	1202.6 (14)	3048.9 (10)	1362.0 (13)	93
S(62)	−1530.8 (14)	2125.3 (10)	5564.0 (13)	86
S(63)	1459.3 (13)	−318.0 (8)	3716.2 (11)	76
S(64)	−3009.6 (11)	1849.2 (8)	1736.3 (11)	68
C(41)	−1075 (4)	366 (2)	2776 (4)	47
C(42)	−962 (4)	390 (3)	4164 (4)	60
C(43)	−1238 (4)	−273 (3)	4000 (4)	75
C(44)	−937 (4)	623 (3)	1963 (3)	48
C(45)	−433 (4)	1334 (3)	1105 (4)	55
C(46)	−944 (5)	903 (4)	501 (4)	81
C(51)	559 (4)	3001 (3)	3824 (4)	52
C(52)	−784 (5)	3178 (3)	3110 (4)	76
C(53)	−368 (5)	3822 (3)	3165 (5)	93
C(54)	1316 (4)	2609 (3)	4166 (3)	53
C(55)	2053 (4)	1708 (3)	4394 (4)	60
C(56)	2709 (4)	2157 (3)	4844 (4)	78
C(61)	899 (4)	2480 (3)	1906 (4)	49
C(62)	−895 (4)	1881 (3)	4906 (4)	50
C(63)	1154 (4)	381 (3)	3508 (3)	47
C(64)	−2083 (4)	1883 (2)	2319 (4)	46

Table IV. Fractional Coordinates ($\times 10^5$) and Equivalent Thermal Parameters ($\times 10^3$) for $ZrCl_4(bt)_2 \cdot 2CH_3CN$

atom	*x*	*y*	*z*	U_{eq}
Zr	0	11 481 (2)	$^1/_4$	30
Cl(1)	7 048 (6)	16 584 (5)	43 603 (5)	46
Cl(2)	84 005 (5)	6 378 (5)	26 620 (6)	43
S(1)	58 950 (8)	30 370 (5)	36 753 (7)	57
S(2)	12 719 (7)	42 486 (5)	29 216 (8)	59
N(1)	55 637 (16)	47 624 (14)	35 358 (17)	37
N(2)	9 676 (16)	25 303 (14)	25 917 (17)	38
C(11)	53 461 (20)	40 197 (16)	30 498 (21)	37
C(12)	63 128 (28)	46 424 (22)	46 174 (26)	52
C(13)	65 048 (28)	36 504 (23)	48 789 (27)	55
C(21)	5 451 (21)	32 789 (17)	26 035 (22)	40
C(22)	20 842 (25)	26 452 (22)	29 312 (32)	54
C(23)	23 277 (28)	36 173 (24)	28 479 (34)	59
N(31)	61 437 (31)	10 586 (32)	51 745 (37)	119
C(31)	52 963 (36)	11 215 (27)	47 555 (34)	80
C(32)	41 896 (29)	12 027 (29)	42 243 (40)	91

Table V. Fractional Coordinates ($\times 10^4$) for Hydrogen Atoms in $ZrCl_4(bt)_2 \cdot 2CH_3CN$

atom	*x*	*y*	*z*
H(1)	6926 (21)	4888 (19)	4647 (22)
H(2)	6092 (20)	4963 (19)	5113 (21)
H(3)	7272 (21)	3517 (18)	5170 (21)
H(4)	6040 (21)	3508 (18)	5291 (22)
H(5)	2380 (21)	2423 (19)	3621 (22)
H(6)	2334 (20)	2305 (19)	2479 (23)
H(7)	2875 (21)	3765 (19)	3304 (22)
H(8)	2348 (20)	3795 (18)	2116 (22)
H(31)[a]	3891	1095	4734
H(32)[a]	3978	760	3646
H(33)[a]	4041	1824	3926

[a] Hydrogen atoms on the acetonitrile placed at idealized positions and not refined.

Table VI. Selected Interatomic Distances (Å) in the Coordination Polyhedron for $ZrCl_4(bt)_2$

bond	dist	bond	dist	edge[a]
Zr–Cl(1)	2.497 (1)	Zr–Cl(2)	2.484 (1)	
Zr–N(1)	2.470 (1)	Zr–N(2)	2.456 (2)	
N(1)–N(1′)	2.701 (4)	N(2)–N(2′)	2.667 (4)	*a*
Cl(1)–Cl(2)	3.562 (1)	Cl(1)–Cl(2′)	3.800 (1)	*b*
Cl(1)–N(1)	3.028 (2)	Cl(2)–N(2)	3.022 (2)	*g*
Cl(1)–N(2)	2.916 (2)	Cl(2)–N(1)	3.128 (2)	*h*
Cl(1)–N(2′)	3.122 (2)	Cl(2)–N(1′)	2.908 (2)	*h*

[a] As designated for an ideal dodecahedron.[4]

Zr(2) gave a slightly better fit to the dodecahedron, 0.089-rms separation, than the molecule around Zr(1), 0.100-rms separation; but, both were better than the fits to a square antiprism, 0.123- and 0.117-rms separations for Zr(1) and Zr(2), respectively. In addition, the dihedral angles[31,32] (26.40, 26.40, 42.86, 42.86°) for the normalized polyhedron of $ZrCl_4(bt)_2$ are closer to those for a dodecahedron (four of 29.5°) than for a square antiprism (0.0, 0.0, 52.4, 52.4°) or a bicapped trigonal prism (**3**) (0.0, 21.8, 48.2, 48.2°). Similarly, the dihedral angles for the two normalized molecules of $Zr(NCS)_4(bt)_2$ (44.60, 44.98, 32.70, 14.75°; 46.11, 42.32, 24.40, 24.05°, respectively) are closer to those of a dodecahedron than those of a square antiprism. The dihedral angles also show that the distortion places both $ZrX_4(bt)_2$ complexes on the D_{2d} reaction pathway between a dodecahedron and a square antiprism.

The principal distortion for $ZrCl_4(bt)_2$ from the ideal dodecahedron is a rotation of the *a* edges with respect to each other from the ideal value of 90 to 72.0°. This rotation relieves the interaction between the bulky methylene groups, $C(12)H_2$ and $C(22)H_2$, and the chlorine atoms. The corresponding displacement of the chlorine atoms is much smaller; the Cl(1)ZrCl(1′) plane is still nearly perpendicular, 85.6°, to the

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Table VII. Selected Interatomic Distances (Å) in the Coordination Polyhedra for $Zr(NCS)_4(bt)_2$

bond	dist	bond	dist	edge[a]
Zr(1)–N(11)	2.402 (4)	Zr(1)–N(21)	2.392 (5)	
Zr(1)–N(12)	2.375 (4)	Zr(1)–N(22)	2.411 (4)	
Zr(1)–N(31)	2.156 (5)	Zr(1)–N(32)	2.183 (5)	
Zr(1)–N(33)	2.182 (5)	Zr(1)–N(34)	2.167 (5)	
N(11)–N(12)	2.629 (6)	N(21)–N(22)	2.644 (7)	*a*
N(31)–N(32)	3.174 (6)	N(32)–N(33)	3.057 (7)	*b*
N(33)–N(34)	3.535 (7)	N(34)–N(31)	3.008 (7)	*b*
N(11)–N(32)	2.793 (6)	N(12)–N(34)	2.742 (6)	*g*
N(21)–N(33)	2.743 (7)	N(22)–N(31)	2.796 (6)	*g*
N(11)–N(31)	2.665 (6)	N(11)–N(33)	2.823 (6)	*h*
N(12)–N(31)	2.985 (6)	N(12)–N(33)	2.739 (6)	*h*
N(21)–N(32)	2.996 (7)	N(21)–N(34)	2.791 (6)	*h*
N(22)–N(32)	2.737 (6)	N(22)–N(34)	2.765 (6)	*h*
Zr(2)–N(41)	2.373 (4)	Zr(2)–N(42)	2.378 (4)	
Zr(2)–N(51)	2.374 (5)	Zr(2)–N(52)	2.400 (4)	
Zr(2)–N(61)	2.178 (5)	Zr(2)–N(62)	2.161 (5)	
Zr(2)–N(63)	2.168 (5)	Zr(2)–N(64)	2.187 (5)	
N(41)–N(42)	2.627 (6)	N(51)–N(52)	2.645 (7)	*a*
N(61)–N(63)	3.112 (7)	N(63)–N(62)	3.356 (7)	*b*
N(62)–N(64)	2.985 (7)	N(64)–N(61)	3.347 (7)	*b*
N(41)–N(62)	2.756 (6)	N(42)–N(61)	2.755 (7)	*g*
N(51)–N(64)	2.769 (7)	N(52)–N(63)	2.732 (7)	*g*
N(41)–N(63)	2.659 (6)	N(41)–N(64)	2.901 (6)	*h*
N(42)–N(63)	2.958 (6)	N(42)–N(64)	2.669 (6)	*h*
N(51)–N(61)	2.695 (6)	N(51)–N(62)	2.834 (6)	*h*
N(52)–N(61)	2.867 (6)	N(52)–N(62)	2.826 (7)	*h*

[a] As designated for an ideal dodecahedron.[4]

Table VIII. Selected Interatomic Distances (Å) in the Coordination Polyhedra for $ZrCl_4(btz)$

Zr(1)–Cl(11)	2.431 (3)	Zr(2)–Cl(21)	2.408 (3)
Zr(1)–Cl(12)	2.378 (3)	Zr(2)–Cl(22)	2.374 (3)
Zr(1)–Cl(13)	2.374 (3)	Zr(2)–Cl(23)	2.430 (2)
Zr(1)–Cl(14)	2.370 (3)	Zr(2)–Cl(24)	2.381 (2)
Zr(1)–N(11)	2.292 (7)	Zr(2)–N(21)	2.314 (7)
Zr(1)–N(12)	2.301 (7)	Zr(2)–N(22)	2.293 (7)
N(11)–N(12)	2.609 (10)	N(21)–N(22)	2.608 (9)
Cl(11)–N(11)	3.107 (7)	Cl(21)–N(21)	3.215 (7)
Cl(11)–N(12)	3.223 (8)	Cl(21)–N(22)	3.144 (7)
Cl(13)–N(11)	3.283 (8)	Cl(23)–N(21)	3.106 (7)
Cl(13)–N(12)	3.107 (7)	Cl(23)–N(22)	3.165 (7)
Cl(12)–Cl(14)	3.731 (4)	Cl(22)–Cl(24)	3.679 (3)
Cl(11)–Cl(12)	3.492 (3)	Cl(21)–Cl(22)	3.548 (4)
Cl(11)–Cl(14)	3.450 (4)	Cl(21)–Cl(24)	3.555 (3)
Cl(13)–Cl(12)	3.524 (4)	Cl(23)–Cl(22)	3.511 (3)
Cl(13)–Cl(14)	3.463 (4)	Cl(23)–Cl(24)	3.496 (3)
N(11)–Cl(12)	3.384 (8)	N(21)–Cl(24)	3.455 (7)
N(12)–Cl(14)	3.426 (8)	N(22)–Cl(22)	3.437 (8)

Table IX. Interatomic Distances (Å) and Angles (deg) for the Isothiocyanate Ligands in $Zr(NCS)_4(bt)_2$

N(31)–C(31)	1.160 (6)	Zr(1)N(31)C(31)	157.3 (3)
N(32)–C(32)	1.139 (6)	Zr(1)N(32)C(32)	149.9 (3)
N(33)–C(33)	1.166 (6)	Zr(1)N(33)C(33)	174.0 (2)
N(34)–C(34)	1.162 (6)	Zr(1)N(34)C(34)	153.6 (3)
N(61)–C(61)	1.141 (6)	Zr(2)N(61)C(61)	156.2 (3)
N(62)–C(62)	1.159 (6)	Zr(2)N(62)C(62)	154.6 (3)
N(63)–C(63)	1.174 (6)	Zr(2)N(63)C(63)	156.5 (3)
N(64)–C(64)	1.171 (6)	Zr(2)N(64)C(64)	156.7 (3)
C(31)–S(31)	1.604 (6)	N(31)C(31)S(31)	179.7 (3)
C(32)–S(32)	1.617 (6)	N(32)C(32)S(32)	178.8 (3)
C(33)–S(33)	1.611 (6)	N(33)C(33)S(33)	179.1 (3)
C(34)–S(34)	1.608 (6)	N(34)C(34)S(34)	179.0 (3)
C(61)–S(61)	1.618 (7)	N(61)C(61)S(61)	179.3 (3)
C(62)–S(62)	1.617 (6)	N(62)C(62)S(62)	179.0 (3)
C(63)–S(63)	1.605 (6)	N(63)C(63)S(63)	178.0 (3)
C(64)–S(64)	1.600 (6)	N(64)C(64)S(64)	179.2 (3)

Table X. Interatomic Distances (Å) for the 2,2′-Bi-2-thiazoline Ligands in $ZrCl_4(bt)_2$ and $Zr(NCS)_4(bt)_2$

	$ZrCl_4(bt)_2$[a]	$Zr(NCS)_4(bt)_2$[b]		
bond\ring	a,b	a–d	e–h	av
C(1)–C(1′)	1.468 (5)	1.471 (7)	1.479 (7)	
	1.461 (5)	1.466 (7)	1.481 (8)	1.471 (8)
C(1)–S	1.729 (2)	1.717 (6)	1.722 (6)	
	1.737 (2)	1.726 (5)	1.742 (5)	
		1.725 (6)	1.722 (6)	
		1.732 (6)	1.728 (6)	1.728 (7)
C(1)–N	1.273 (3)	1.289 (6)	1.276 (6)	
	1.276 (3)	1.276 (6)	1.265 (6)	
		1.276 (6)	1.282 (6)	
		1.283 (6)	1.265 (6)	1.276 (7)
N–C(2)	1.475 (3)	1.473 (6)	1.476 (6)	
	1.482 (4)	1.483 (6)	1.474 (6)	
		1.471 (7)	1.465 (7)	
		1.458 (7)	1.462 (6)	1.472 (8)
C(2)–C(3)	1.527 (4)	1.515 (8)	1.509 (8)	
	1.499 (4)	1.518 (7)	1.502 (8)	
		1.499 (8)	1.528 (9)	
		1.522 (7)	1.514 (8)	1.513 (11)
S–C(3)	1.807 (3)	1.791 (6)	1.795 (6)	
	1.804 (4)	1.805 (6)	1.784 (7)	
		1.781 (7)	1.746 (8)	
		1.795 (6)	1.801 (7)	1.791 (18)

[a] In $ZrCl_4(bt)_2$ ring a = S(1)C(11)N(1)C(12)C(13) and ring b = S(2)C(21)N(2)C(22)C(23). [b] In $Zr(NCS)_4(bt)_2$ ring a = S(11)C(11)N(11)C(12)C(13), ring b = S(12)C(14)N(12)C(15)-C(16), ring c = S(21)C(21)N(21)C(22)C(23), ring d = S(22)C(24)-N(22)C(25)C(26), ring e = S(41)C(41)N(41)C(42)C(43), ring f = S(42)C(44)N(42)C(45)C(46), ring g = S(51)C(51)N(51)C(52)-C(53), and ring h = S(52)C(54)N(52)C(55)C(56).

Cl(Z)ZrCl(2′) plane as would be found in an ideal dodecahedron. Even after the distortion, this interaction is still quite short; the Cl(1)···HC(12) distance is 2.70 Å, and the matching Cl(2)···HC(22) distance is 2.71 Å. Both are less than the normal Cl–H van der Waals[33] contact distance, 2.95 Å. Although the distortions in the two molecules of $Zr(NCS)_4(bt)_2$ are more complex, the principal distortion can still be described as a rotation of the *a* edges of an ideal dodecahedron with respect to each other. The angle between the planes N(11)Zr(1)N(12) and N(21)Zr(1)N(22) is 73.4° and is 83.1° for the planes N(41)Zr(2)N(42) and N(51)Zr(2)N(52) compared to 90° for an ideal dodecahedron. As was the case for $ZrCl_4(bt)_2$, this distortion relieves the close contacts between the methylene groups and the halide ligands. In contrast to the situation for $ZrCl_4(bt)_2$, the nonbonded interligand contacts in $Zr(NCS)_4(bt)_2$ are not tight; the N···N distances in the coordination polyhedra are quite similar to those found in $Zr(NCS)_4(bpy)_2$[20]. Moreover, the differences between the two inequivalent molecules of $Zr(NCS)_4(bt)_2$ would imply a greater flexibility than for $ZrCl_4(bt)_2$ and is consistent with the lessened ligand–ligand repulsions.

The bulkiness of the ligands for $ZrCl_4(bt)_2$ has resulted in very long Zr–L bonds. The average Zr–N bond, 2.46 Å, is considerably longer than for six-coordinate $ZrCl_4(btz)$, 2.30 Å, and longer than for eight-coordinate $Zr(NCS)_4(bpy)_2$,[20] 2.41 Å, or $Zr(NCS)_4(bt)_2$, 2.39 Å, both of which have smaller ligands; both the bpy and bt complexes also have similar Zr–NCS bond lengths, 2.18 and 2.17 Å, respectively. Similarly, the Zr–Cl bonds for $ZrCl_2(bt)_2$, 2.49 Å, are longer than for $ZnCl_4(btz)$, 2.3. Å. In fact, these two molecules show the extremes for Zr–Cl bond lengths; the shortest previously reported is 2.39 Å for $ZrCl[N(SiMe_3)_2]_3$[31] and the longest previously reported is 2.47 Å for $ZrCl(acac)_3$.[32]

The cis octahedra for $ZrCl_4(btz)$ also show distortions due to the bulkiness of the ligands. Kepert[33] has defined two characteristics angles, ϕ_C and ϕ_E, of the cis octahedra (Figure 5) and predicted their values according to the normalized bite of the bidentate ligand. In the present case the expected values of ϕ_C and ϕ_E are 93 and 133°, respectively, which are much

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Table XI. Interatomic Angles (deg) for the 2,2′-Bi-2-thiazoline Ligands in $ZrCl_4(bt)_2$ and $Zr(NCS)_4(bt)_2$

	$ZrCl_4(bt)_2$[a]	$Zr(NCS)_4(bt)_2$[b]		
angle\ring	a,b	a–d	e–h	av
C(1)NC(2)	111.2 (4)	110.5 (4)	109.9 (4)	
	110.0 (5)	111.1 (4)	112.2 (4)	
		110.0 (4)	110.0 (5)	
		110.7 (4)	111.3 (4)	110.7 (8)
NC(2)C(3)	111.0 (5)	110.6 (5)	111.1 (5)	
	110.4 (6)	111.0 (5)	109.4 (5)	
		111.3 (5)	108.7 (6)	
		109.5 (5)	110.6 (6)	110.4 (9)
C(2)C(3)S	106.7 (5)	108.5 (5)	107.3 (5)	
	106.3 (6)	107.6 (4)	109.8 (5)	
		108.0 (5)	107.8 (5)	
		106.6 (5)	108.3 (5)	107.7 (10)
C(3)SC(1)	89.9 (1)	89.3 (3)	89.1 (2)	
	88.9 (1)	90.0 (2)	88.6 (3)	
		89.3 (3)	89.1 (3)	
		88.8 (2)	88.6 (3)	89.2 (5)
SC(1)N	120.3 (4)	120.8 (4)	120.9 (4)	
	119.8 (4)	120.4 (4)	119.9 (4)	
		120.6 (4)	119.9 (5)	
		119.7 (4)	121.1 (4)	120.6 (7)
SC(1)C(1′)	121.0 (5)	122.6 (4)	123.6 (4)	
	122.3 (5)	122.9 (4)	122.2 (4)	
		121.8 (4)	123.1 (4)	
		123.0 (4)	121.4 (4)	122.4 (8)
NC(1)C(1′)	118.7 (6)	116.5 (5)	117.5 (5)	
	117.9 (6)	116.7 (4)	117.9 (4)	
		117.5 (5)	116.9 (5)	
		117.3 (5)	117.4 (5)	117.4 (6)
C(1)NZr	117.6 (4)	119.0 (3)	120.0 (3)	
	118.6 (4)	120.1 (3)	118.8 (4)	
		119.6 (3)	119.4 (4)	
		118.7 (4)	118.8 (4)	119.2 (9)
C(2)NZr	129.8 (3)	129.8 (3)	129.3 (3)	
	129.0 (3)	128.1 (3)	127.6 (3)	
		130.3 (3)	130.4 (3)	
		130.2 (3)	129.8 (3)	129.4 (9)

[a] In $ZrCl_4(bt)_2$ ring a = S(1)C(11)N(1)C(12)C(13) and ring b = S(2)C(21)N(2)C(22)C(23). [b] In $Zr(NCS)_4(bt)_2$ ring a = S(11)-C(11)N(11)C(12)C(13), ring b = S(12)C(14)N(12)C(15)C(16), ring c = S(21)C(21)N(21)C(22)C(23), ring d = S(22)C(24)N(22)-C(25)C(26), ring e = S(41)C(41)N(41)C(42)C(43), ring f = S(42)-C(44)N(42)C(45)C(46), ring g = S(51)C(51)N(51)C(52)C(53), and ring h = S(52)C(54)N(52)C(55)C(56).

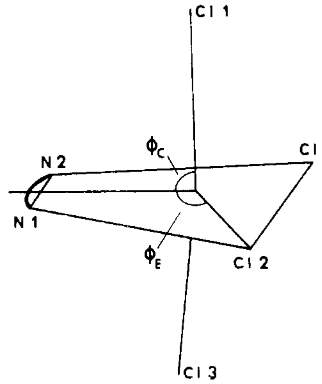

Figure 5. Diagram of the coordination sphere of Zr(1) in $ZrCl_4(btz)$. Characteristic angles ϕ_C and ϕ_E are indicated. The coordinated sphere for Zr(2) is similar.

larger than actually found, 84.1 and 128.1°, respectively, for Zr(1) and 82.6 and 128.9°, respectively, for Zr(2). Clearly, the repulsion between the four Cl atoms is mostly responsible for this distortion, and the size and shape of the btz ligand has little effect except to prevent the formation of an eight-coordinate complex.

The bond distances and angles within the polyatomic ligands were all found to be near their expected values. The NCS groups (Table IX) are all linear with expected bond lengths; however, they do not form linear M–NCS groups. The interactions with neighboring molecules have led to bent, 150–174°, M–N–C bonds that are not dissimilar to those found in other structures.[20] The bt and btz ligands (Tables X–XII) both have similar bonding patterns; the N–C(1) bond has definite double-bond character, and some conjugation occurs, shortening both the C(1)–C(1′) and C(1)–S bonds. All the other bonds appear to be normal single bonds. The bond angles in the five-membered thiazoline rings are smaller than their equivalents in the six-membered thiazine rings; the differences are expected from ring size considerations. The thiazoline rings are quite flat; the root-mean-square displacements of the atoms from their five-atom best planes are 0.10–0.30 Å. Apparently the small CSC angles, ~90°, allow the bt rings to have a planar conformation rather than the more common "envelope" arrangement found for five-membered rings. As expected, the thiazine rings are not planar, with the two methylene atoms, C(3) and C(4), displaced to opposite sides of the six-atom best plane. This displacement accounts for the principal difference between the two inequivalent molecules in the $ZrCl_4(btz)$ structure. For Zr(1)

Table XII. Interatomic Distances (Å) and Angles (deg) for the 2,2′-Bi-2-thiazine Ligands[a] in $ZrCl_4(btz)$

ring	a	b	c	d	av
			Bond		
C(1)–N	1.288 (10)	1.277 (10)	1.277 (9)	1.281 (10)	1.281 (11)
C(1)–S	1.717 (9)	1.721 (9)	1.730 (9)	1.737 (9)	1.726 (10)
N–C(2)	1.466 (11)	1.465 (10)	1.475 (10)	1.456 (10)	1.466 (12)
C(2)–C(3)	1.535 (13)	1.512 (13)	1.520 (11)	1.478 (13)	1.511 (14)
C(3)–C(4)	1.481 (13)	1.451 (13)	1.474 (11)	1.447 (13)	1.463 (14)
C(4)–S	1.781 (12)	1.789 (10)	1.808 (9)	1.802 (10)	1.795 (12)
C(1)–C(1′)	1.522 (11)		1.497 (11)		1.510 (16)
			Angle		
ZrNC(1)	119.4 (6)	119.1 (6)	119.0 (5)	120.0 (5)	119.4 (6)
ZrNC(2)	120.8 (5)	120.6 (5)	120.7 (5)	119.3 (5)	120.4 (6)
C(1)NC(2)	118.3 (6)	120.2 (6)	120.0 (6)	120.7 (6)	119.8 (7)
NC(1)C(1′)	113.6 (8)	116.1 (8)	115.8 (8)	115.5 (8)	115.3 (9)
NC(1)S	131.1 (6)	129.5 (6)	128.0 (6)	128.9 (6)	129.4 (7)
SC(1)C(1′)	115.3 (7)	114.4 (7)	116.2 (6)	115.6 (7)	115.4 (8)
C(1)SC(4)	102.3 (5)	102.8 (4)	102.8 (4)	101.2 (4)	102.3 (5)
SC(4)C(3)	110.5 (8)	111.8 (8)	114.0 (7)	113.1 (8)	112.4 (9)
C(2)C(3)C(4)	112.4 (8)	115.1 (8)	111.4 (8)	114.3 (9)	113.3 (10)
C(3)C(2)N	116.3 (8)	114.3 (8)	112.7 (7)	117.9 (8)	115.3 (9)

[a] In $ZrCl_4(btz)$ ring a = N(11)S(11)C(11)C(12)C(13)C(14), ring b = N(12)S(12)C(15)C(16)C(17)C(18), ring c = N(21)S(21)C(21)C(22)-C(23)C(24), and ring d = N(22)S(22)C(25)C(26)C(27)C(28).

these displacements give the molecule a pseudo-mirror-plane passing through Zr(1)Cl(11)Cl(13) and the C(11)–C(15) bond while for Zr(2) the result is a pseudo twofold axis passing through Zr(2) and the midpoint of the C(21)–C(25) bond. Clearly, there is sufficient flexibility in this molecule to accommodate both arrangements, and the structure uses both to give efficient molecular packing.

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Registry No. $ZrCl_4(btz)$, 92315-30-5; $Zr(NCS)_4(bt)_2$, 92315-31-6; $ZrCl_4(bt)_2 \cdot 2CH_3CN$, 92315-33-8.

Supplementary Material Available: Unit cell diagrams and listings of calculated hydrogen positions, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (95 pages). Ordering information is given on any current masthead page.

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2,6-Bis(diphenylphosphino)pyridine as a Bridging Ligand in Planar Complexes of Platinum(II) and Palladium(II)

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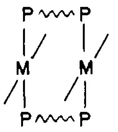
The reactions between 2,6-bis(diphenylphosphino)pyridine and (1,5-cyclooctadiene)MX_2 (M = Pd or Pt; X = Cl, Br, or I) have been studied by $^{31}P\{^1H\}$ NMR spectroscopy and product isolation. With palladium *cis,cis,trans*-$Pd_3[\mu\text{-}(Ph_2P)_2py]_3Cl_6$ forms in high yield and is remarkably stable toward conversion to other isomers or polymeric forms. With platinum, complex mixtures form from which pure compounds can be separated. The structures of two of these have been determined by X-ray diffraction. *cis,cis*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2Cl_4 \cdot 6CH_2Cl_2$ crystallizes in the space group $P2_1/c$ (No. 14) with cell dimensions (at 140 K) a = 16.17 (4) Å, b = 14.60 (4) Å, c = 16.36 (5) Å, β = 110.9 (2)°, and Z = 2. The structure was refined to R = 0.066 for 3005 reflections and 465 parameters. *trans,trans*-$Pt_2[\mu\text{-}(Ph_2P)_2py]_2I_4 \cdot 2CH_2Cl_2$ crystallizes in the space group $C2/c$ (No. 15) with unit cell dimensions (at 140 K) a = 24.093 (7) Å, b = 21.544 (6) Å, c = 12.287 (3) Å, β = 95.08 (2)°, and Z = 4. The structure was refined to R = 0.056 for 3102 reflections and 325 parameters.

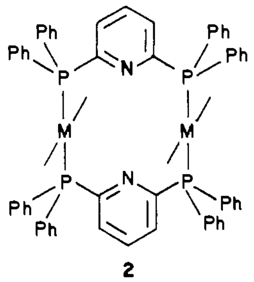
Introduction

Bidentate phosphines have proven to be useful in constructing binuclear complexes that can have a variety of interactions between the two metal centers.[2] Study of the binding of small molecules to the cavity between the two metals in these binuclear complexes continues to attract attention.[3] In exploring these binuclear complexes, it is important to establish the range of structural types available and to determine the factors controlling their formation.

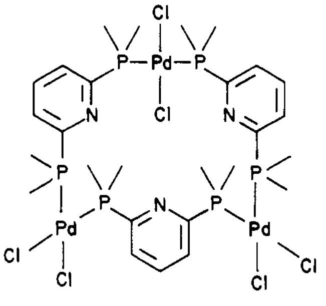
For binuclear complexes, the face-to-face structure **1** represents a now rather common structural type for molecules containing two square-planar metal ions. A number of examples have been structurally characterized.[4-9] With a bis(phosphine) like 2,6-bis(diphenylphosphino)pyridine, $(Ph_2P)_2py$, the formation of such a structure would produce a cavity between the two metal atoms where small molecules and even other metal ions could be bound by a combination of the nucleophilic pyridine nitrogens and the amphoteric metal centers. The rigid nature of $(Ph_2P)_2py$ precludes the formation of a chelate ring with both phosphorus atoms coordinated to a single metal atom.[10-12] This, however, does not ensure that structure **2** will readily form. Mixing $(Ph_2P)_2py$ with (cyclooctadiene)palladium(II) dichloride gives the remarkable trinuclear complex **3** in high yield.[13] This complex contains



1



2



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