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(15) Structure factor calculations and least-squares refinements were carried out using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin), respectively. Other programs include local modifications of Busing and Levy's ORFFE function and error program, and Johnson's ORTEP thermal ellipsoid plotting program.
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Crystal and Molecular Structure of Tetraisothiocyanatobis(2,2'-bipyridine)niobium(IV) and -zirconium(IV)

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The crystal and molecular structures of the eight-coordinate complexes $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $Zr(NCS)_4(C_{10}H_8N_2)_2$ have been determined from single-crystal x-ray intensity data collected by the $\theta-2\theta$ scan technique. In both compounds the metal atoms are coordinated by eight nitrogen atoms, four belonging to the two bidentate 2,2'-bipyridine groups and four belonging to the isothiocyanate ligands. The niobium–nitrogen distances are 2.135 (3) and 2.318 (3) Å, respectively, for the M–NCS and M–2,2'-bpy bonds, while the zirconium–nitrogen distances are 2.182 (2) and 2.412 (2) Å, respectively. The coordination geometries around the metal for both complexes can be obtained by distortions from an idealized D_{2d} dodecahedron along a reaction pathway which retains D_2 symmetry. The degree of distortion correlates with the M–N bond lengths; the smaller niobium complex is sufficiently distorted from a dodecahedron to become a very nearly perfect D_4 square antiprism ($\delta = -2.1, 49.2°$) with the bidentate 2,2'-bipyridines bridging the square faces. The larger zirconium complex is significantly less distorted ($\delta = 4.2, 45.5°$) from the D_{2d} dodecahedron than the niobium complex. Each structure was solved by standard heavy-atom techniques and refined by full-matrix least-squares to final R values of 0.067 (1702 independent observed reflections) for $Nb(NCS)_4(C_{10}H_8N_2)_2$ and 0.056 (1833 independent observed reflections) for $Zr(NCS)_4(C_{10}H_8N_2)_2$. Both compounds crystallize in the orthorhombic space group $Pnnn$, $Z = 2$, with the lattice parameters $a = 7.720$ (4), $b = 13.179$ (7), $c = 13.113$ (4) Å for $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $a = 7.646$ (6), $b = 13.407$ (11), $c = 13.245$ (11) Å for $Zr(NCS)_4(C_{10}H_8N_2)_2$.

Introduction

The elucidation of factors which govern the stereochemistry of eight-coordinate compounds has been the subject of a number of papers.[1-8] Some examples of discrete eight-coordinate complexes and their experimentally assigned stereochemistries are listed in Table I. In general, eight-coordinate complexes are usually classified as either a D_{2d}-$\bar{4}2m$ dodecahedron or a D_{4d}-$\bar{8}2m$ square antiprism. Recently, however, several authors have expressed consternation because many of the usual polyhedron-shape criteria neglect the possibility of a C_{2v} bicapped trigonal prism. Because of these objections, new criteria were proposed which relate the three most common polyhedra along a geometric reaction pathway.[7,8] Several theoretical studies have shown that both the D_{2d} and D_{4d} stereochemistries are equally likely on the basis of crystal field stabilization[3] or minimization of repulsions.[1,3,6] The MX_8 and MX_4Y_4 systems show predominantly dodecahedral stereochemistry, while the $M(A-A)_4$ compounds are divided between dodecahedral and square-antiprismatic structures. The latter observations have been explained in terms of the normalized ligand bite of the symmetrical bidentate ligands.[6] The structure of $Nb[(t\text{-}C_4H_9CO)_2CH]_4$ was recently investigated and found to be a distorted D_4 square antiprism.[9] This structure is significant because it is the first $M(A-A)_4$ system where the bidentate ligands span the l edges of an idealized antiprism.

Eight-coordinate complexes of the type $M(A-A)_2B_4$ are also of interest but have not been as extensively studied as the other systems. Most reported examples are dodecahedral and only a few compounds of this type which even closely approach a square antiprism have been reported, i.e., $W(CH_3)_4[ON(CH_3)NO]_2$[10] and $Zr(SO_4)_2 \cdot 4H_2O$.[11] Thus, in order to elucidate further the factors governing the stereochemical arrangement of ligands in eight-coordinate complexes,

Table I. Examples of Discrete Eight-Coordination

Compd	Type[a]	Ref	Compd	Type	Ref
MX_8			MX_4Y_4		
TaF_8^{3-}	A	13	$Mo(CN)_4(CNR)_4$	D	16
$Mo(CN)_8^{4-}$ [b]	D or A	14, 15	$W(CN)_4(CNR)_4$	D	16
$W(CN)_8^{4-}$ [b]	D or A	14, 15	$H_4Mo[CH_3P(C_6H_5)_2]_4$	D	12
			$Zr(SO_4)_4 \cdot 4H_2O$	A	11
$M(A-A)_4$			$M(A-A)_2B_4$		
$Nb[(t\text{-}BuCO)_2CH]_4$	A	9	$W(Me)_4[ON(Me)NO]_2$ [e]	D–A	10
$Zr(acac)_4$ [b]	A	17	$TiCl_4(diars)_2$	D	22
$Zr(C_2O_4)_4^{4-}$ [c]	D	18	$NbCl_4(diars)_2$	D	23
$Ti[SSCN(C_2H_5)_2]_4$ [d]	D	19			
$Ti(NO_3)_4$ [d]	D	20			
$Zr(IO_3)_4$	A	21			

[a] D = dodecahedron; A = square antiprism. [b] Molecular structure of anion is dependent on counterion. [c] Isostructural with their Hf analogues. [d] Isostructural with the Zr analogues. [e] Intermediate between dodecahedron and antiprism. Half of the molecule appears like an antiprism; the other half, like a dodecahedron.

single-crystal x-ray structure determinations of $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $Zr(NCS)_4(C_{10}H_8N_2)_2$ were undertaken. The coordination polyhedra in both complexes are described using several polyhedron-shape criteria, and the observed stereochemistries are discussed in terms of the interactions between the ligands involved and the effect of the size of the metal atom.

Experimental Section

$Nb(NCS)_4(C_{10}H_8N_2)_2$. Preparation. The preparation of the niobium complex has been reported previously.[24] The procedure was modified in that bipyridine was added to the solution of $K_2Nb(NCS)_6$ in acetonitrile by slow sublimation in a sealed vessel. Suitable red crystals separated from the solution over a period of 1 week. Unlike many compounds of niobium, the crystals resisted hydrolysis indefinitely even when exposed to x-rays in the open air.

Crystal Data and Data Collection. Preliminary precession and Weissenberg photographs displayed *mmm* Laue symmetry and the systematic absences $0kl$ for $k + l = 2n + 1$, $h0l$ for $h + l = 2n + 1$, and $hk0$ for $h + k = 2n + 1$ which uniquely correspond to the centrosymmetric orthorhombic space group *Pnnn*.[25] A total of 51 reflections within the angular range $5° \leq 2\theta \leq 60°$ for Mo Kα radiation were automatically centered on a Syntex $P\bar{1}$ autodiffractometer; a least-squares refinement of the angular settings yielded the lattice parameters $a = 7.720$ (4), $b = 13.179$ (7), $c = 13.113$ (4) Å which for $Z = 2$ gives $\rho_{calcd} = 1.598$ g/cm^{-3} ($\rho_{obsd} = 1.60$ g/cm^{-3}, by flotation in a CCl_4–CBr_4 solution).

The diffraction intensities were measured on a well-formed crystal of approximate dimensions 0.5 × 0.3 × 0.2 mm, mounted on a glass fiber with the long dimension of the crystal (along the *a* axis) tilted about 45° off the fiber axis, using Zr-filtered Mo Kα radiation within the range $3° \leq 2\theta \leq 60°$ and θ–2θ scans of variable rate and range. The scanning rate was 1° min^{-1} for most reflections but was increased up to 12° min^{-1} for those of highest intensity. The base scan range of 2.0° was varied slightly to take account of spectral dispersion, and background measurements lasting 0.25 of the scan time were made at each end of the scan. A total of 2405 independent reflections were investigated with the Mo tube operating at 25 mA and 40 kV. An additional 231 reflections in the range of $3° \leq 2\theta \leq 25°$ were reinvestigated at 15 mA and 40 kV to obtain reliable intensities for the strongest reflections. After applying a least-squares scaling procedure,[26] a total of 1702 reflections were retained as objectively observed with $|F_o| > 0.675\sigma_F$, $\sigma_F = 0.025|F_o| + (C + k^2B)^{1/2}R/(2|F_o|Lp)$ where C is the total count in a scan taken at the rate R and k is the ratio of scanning time to the time for the total background count B. Periodic monitoring of three reflections showed a maximum 10% decrease in intensity throughout the data collection, and thus the observed structure factors were linearly corrected for this loss of intensity. The usual Lorentz and polarization corrections were applied and analytic absorption corrections[27] were made for a linear absorption coefficient of 7.4 cm^{-1}.

Structure Solution and Refinement. Since the niobium atoms must be at the special positions with 222 point symmetry, it was only necessary to locate one thiocyanate group and half of a bipyridyl ligand. A three-dimensional Patterson map was used to obtain the apparent positions of the nitrogen, carbon, and sulfur of the thiocyanate group and the bipyridine nitrogen. A Fourier synthesis based on these atoms indicated the positions of all other nonhydrogen atoms. Four cycles of least-squares refinement[28] of the model with isotropic thermal motion converged to a standard residual of $R = 0.141$, and the weighted residual, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, was 0.130 for unit weights. The atomic scattering factors for Nb^0, S^0, N^0, and C^0 calculated by Cromer and Mann[29] were used with real and imaginary anomalous dispersion corrections[30] applied for Nb and S. A model with anisotropic temperature factors was refined to give residuals $R = 0.091$ and R_w (unit weights) = 0.086. A difference Fourier showed peaks ranging from 0.3 to 0.6 e/A^3 in positions reasonable for bipyridine hydrogen atoms, and no other large peaks were evident. Two more cycles of least-squares refinement with fixed hydrogen coordinates gave residuals of $R = 0.083$ and R_w (unit weights) = 0.070. Four final cycles of refinement, varying both hydrogen coordinates and individual isotropic temperature factors as well as all other parameters, converged with $R = 0.067$ and R_w ($w = 1/\sigma_F^2$) = 0.048. On the final refinement cycle, no parameter shift was greater than 0.02 esd. A difference Fourier synthesis using these final parameters showed no peaks greater than 0.17 e/A^3.

$Zr(NCS)_4(C_{10}H_8N_2)_2$. Preparation. The preparation of the zirconium complex was carried out in much the same manner as the niobium complex. The bipyridine was slowly introduced by sublimation into an acetonitrile solution of $Zr(NCS)_4 \cdot 2CH_3CN$ in a sealed vessel. Suitable transparent crystals separated from solution after about 1 month. Again, the crystals resisted hydrolysis indefinitely.

Crystal Data and Data Collection. Preliminary investigation of a suitable crystal of approximate dimensions 0.4 × 0.3 × 0.3 mm by precession film techniques indicated that the zirconium complex was isomorphous with the niobium compound. A total of 59 reflections within the angular range $5° \leq 2\theta \leq 60°$ for Mo Kα radiation were automatically centered; a least-squares refinement of the angular settings yielded the lattice parameters $a = 7.646$ (6), $b = 13.407$ (11), $c = 13.245$ (11) Å which for $Z = 2$ gives $\rho_{calcd} = 1.554$ g/cm^3 ($\rho_{obsd} = 1.56$ g/cm^3, by flotation in a CCl_4–CBr_4 solution).

Diffraction intensities were measured for 2452 independent reflections within the range $3° \leq 2\theta \leq 60°$ for monochromated Mo Kα radiation using θ–2θ scans of variable rate and range. The scanning rate was 1°/min for most reflections but was increased up to 12°/min for those of higher intensity. The base scan range of 1.4° was varied slightly to take account of spectral dispersion, and background measurements lasting 0.25 of the scan time were made at each end of the scan. Periodic monitoring of three reflections showed no decrease in intensity throughout the entire data collection. A total of 1833 reflections were retained as objectively observed with $|F_o| > 0.675\sigma_F$, $\sigma_F = 0.025|F_o| + (C + k^2B)^{1/2}R/(2|F_o|Lp)$ where C is the total count in a scan taken at the rate R and k is the ratio of scanning time to the time for the total background count B. The usual Lorentz and polarization corrections for monochromated radiation[31] were applied and analytical absorption corrections[27] were made for a linear absorption coefficient of 7.2 cm^{-1}.

Structure Solution and Refinement. The position of the zirconium atom is at the special position with 222 point symmetry and, as in the niobium complex, one thiocyanate group and half of a bipyridyl ligand completely determine the structure. A Fourier synthesis[32] using the zirconium position indicated positions for all nonhydrogen atoms. At this point it became evident that the atom positions were quite similar to those in the niobium complex. Three cycles of full-matrix least-squares refinement of the model with isotropic thermal motion converged to a standard residual of $R = 0.164$; and the weighted residual, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, was 0.182 for $w = 1/\sigma_F^2$. The atomic scattering factors for Zr^0, S^0, N^0, and C^0 from published tables[33] were used with real and imaginary anomalous dispersion corrections[33] applied for Zr and S. A model with anisotropic thermal motion was refined to give the residuals $R = 0.090$ and R_w ($w = 1/\sigma_F^2$) = 0.098. A difference Fourier showed peaks ranging from 0.3 to 0.6 e/A^3 in positions reasonable for bipyridine hydrogen atoms. Four final cycles of least-squares refinement, varying both hydrogen coordinates and individual isotropic temperature factors

Table II. Final Positional Parameters[a] and Isotropic Temperature Parameters with Esd's for $Nb(NCS)_4(C_{10}H_8N_2)_2$

Atom[b]	x/a	y/b	z/c	U_{Iso}, $Å^2$
Nb[c]	0.2500	0.2500	0.2500	
N1	0.3964 (4)	0.3032 (2)	0.3773 (2)	
N2	0.4012 (3)	0.1062 (2)	0.2996 (2)	
S1	0.5232 (1)	0.3534 (1)	0.5674 (1)	
C1	0.4485 (4)	0.3250 (3)	0.4573 (2)	
C2	0.1680 (4)	0.4856 (3)	0.2780 (2)	
C3	0.0868 (5)	0.5741 (3)	0.3102 (3)	
C4	−0.0707 (5)	0.5706 (3)	0.3600 (3)	
C5	−0.1441 (5)	0.4770 (4)	0.3772 (3)	
C6	−0.0568 (5)	0.3917 (3)	0.3462 (3)	
H3	0.140 (4)	0.637 (2)	0.299 (3)	0.016 (9)
H4	−0.130 (5)	0.633 (3)	0.374 (3)	0.040 (12)
H5	−0.253 (5)	0.471 (3)	0.410 (2)	0.023 (9)
H6	−0.108 (4)	0.327 (2)	0.359 (2)	0.012 (8)

[a] Atomic coordinates are given only for the unique portion of the molecule. [b] Value in parentheses is the estimated standard deviation in the last significant figure in this and all following tables. [c] The niobium atoms fall at special positions at the intersection of three twofold axes.

Table III. Final Positional Parameters[a] and Isotropic Thermal Parameters with Esd's for $Zr(NCS)_4(C_{10}H_8N_2)_2$

Atom	x/a	y/b	z/c	U_{Iso}, $Å^2$
Zr[b]	0.2500	0.2500	0.2500	
N1	0.4117 (4)	0.3012 (2)	0.3756 (2)	
N2	0.4015 (3)	0.1009 (2)	0.3023 (2)	
S1	0.5279 (1)	0.3525 (1)	0.5650 (1)	
C1	0.4602 (3)	0.3234 (2)	0.4554 (2)	
C2	0.1673 (3)	0.4890 (2)	0.2788 (2)	
C3	0.0863 (4)	0.5772 (2)	0.3081 (2)	
C4	−0.0718 (4)	0.5736 (3)	0.3589 (2)	
C5	−0.1446 (4)	0.4823 (3)	0.3791 (3)	
C6	−0.0573 (4)	0.3979 (2)	0.3503 (2)	
H3	0.133 (4)	0.643 (2)	0.286 (2)	0.034 (7)
H4	−0.132 (5)	0.640 (2)	0.381 (3)	0.056 (10)
H5	−0.260 (5)	0.474 (3)	0.411 (3)	0.058 (10)
H6	−0.111 (3)	0.330 (2)	0.360 (2)	0.026 (6)

[a] Atomic coordinates are only given for the unique portion of the molecule. [b] The zirconium atoms fall at special positions at the intersection of three twofold axes.

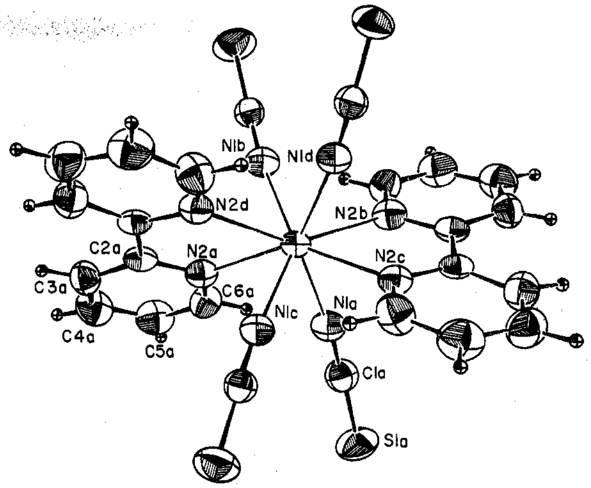


Figure 1. Perspective view of $Nb(NCS)_4(C_{10}H_8N_2)_2$. The numbering scheme for the atoms is defined. The Zr analog is visually identical.

as well as all other parameters, converged with $R = 0.056$ and R_w ($w = 1/\sigma_F^2$) = 0.053. On the final refinement cycle, no parameter shift was greater than 0.02 esd. A difference Fourier synthesis using these final parameters showed no peak greater than 0.4 e/$Å^3$.

Results

Final atomic coordinates and thermal parameters are presented in Tables II and IV for $Nb(NCS)_4(C_{10}H_8N_2)_2$ and Tables III and V for $Zr(NCS)_4(C_{10}H_8N_2)_2$ along with the estimated standard deviations derived from the least-squares analysis. The perspective view of the molecule shown in Figure 1 shows the essential spatial features of the niobium molecule (the zirconium molecule appears quite identical to the eye). Each atom is represented by an ellipsoid consistent with anisotropic thermal parameters in Table IV and each unique atom is labeled with a literal and a numerical subscript; the literal subscript identifies the particular bipyridine or isothiocyanate ligand (a, b, c, or d). A stereoview of the packing for the $Nb(NCS)_4(C_{10}H_8N_2)_2$ molecules is shown in Figure

Table IV. Anisotropic Thermal Parameters for $Nb(NCS)_4(C_{10}H_8N_2)_2$

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb[b]	0.0454 (3)	0.0423 (3)	0.0276 (2)	0.0	0.0	0.0
N1	0.0631 (18)	0.0496 (17)	0.0407 (15)	0.0005 (16)	−0.0104 (14)	−0.0003 (14)
N2	0.0391 (14)	0.0492 (17)	0.0369 (14)	0.0030 (13)	−0.0010 (12)	−0.0016 (13)
S1	0.0761 (7)	0.0852 (8)	0.0489 (6)	0.0030 (6)	−0.0234 (5)	−0.0151 (5)
C1	0.0427 (18)	0.0430 (19)	0.0415 (18)	0.0043 (15)	−0.0013 (15)	−0.0006 (15)
C2	0.0408 (17)	0.0478 (18)	0.0293 (14)	0.0007 (15)	−0.0064 (12)	−0.0002 (13)
C3	0.0532 (22)	0.0485 (22)	0.0515 (21)	0.0025 (19)	−0.0088 (18)	−0.0030 (18)
C4	0.0548 (24)	0.0622 (27)	0.0590 (23)	0.0160 (22)	0.0023 (20)	−0.0064 (21)
C5	0.0463 (22)	0.0755 (29)	0.0589 (24)	0.0110 (22)	0.0095 (18)	−0.0005 (21)
C6	0.0481 (21)	0.0567 (24)	0.0608 (23)	0.0011 (20)	0.0089 (19)	0.0063 (20)

[a] These temperature factors enter the expression for the structure in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$. [b] U_{12}, U_{13}, and U_{23} are zero for the niobium atom because it lies at a special position.

Table V. Anisotropic Thermal Parameters for $Zr(NCS)_4(C_{10}H_8N_2)_2$

Atom	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zr[b]	0.0628 (3)	0.0508 (3)	0.0344 (2)	0.0	0.0	0.0
N1	0.0953 (18)	0.0620 (14)	0.0512 (12)	−0.0015 (14)	−0.0153 (12)	−0.0022 (11)
N2	0.0560 (12)	0.0565 (12)	0.0462 (11)	0.00010 (10)	−0.0015 (9)	0.0001 (9)
S1	0.0911 (6)	0.0944 (6)	0.0566 (4)	0.0046 (5)	−0.0238 (4)	−0.0171 (4)
C1	0.0548 (14)	0.0485 (13)	0.0504 (13)	0.0044 (11)	−0.0050 (11)	−0.0019 (11)
C2	0.0515 (13)	0.0546 (13)	0.0380 (10)	0.0008 (11)	−0.0071 (10)	−0.0004 (9)
C3	0.0624 (16)	0.0588 (16)	0.0578 (15)	0.0026 (13)	−0.0048 (13)	−0.0009 (13)
C4	0.0658 (18)	0.0732 (19)	0.0714 (19)	0.0168 (16)	0.0004 (15)	−0.0073 (16)
C5	0.0600 (18)	0.0834 (22)	0.0735 (20)	0.0105 (16)	0.0120 (15)	0.0025 (16)
C6	0.0622 (17)	0.0698 (19)	0.0714 (18)	0.0011 (15)	0.0123 (15)	0.0056 (15)

[a] These temperature factors enter the expression for the structure in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + ... + 2U_{23}klb^*c^*)]$. [b] U_{12}, U_{13}, and U_{23} are zero for the zirconium atom because it lies at a special position.

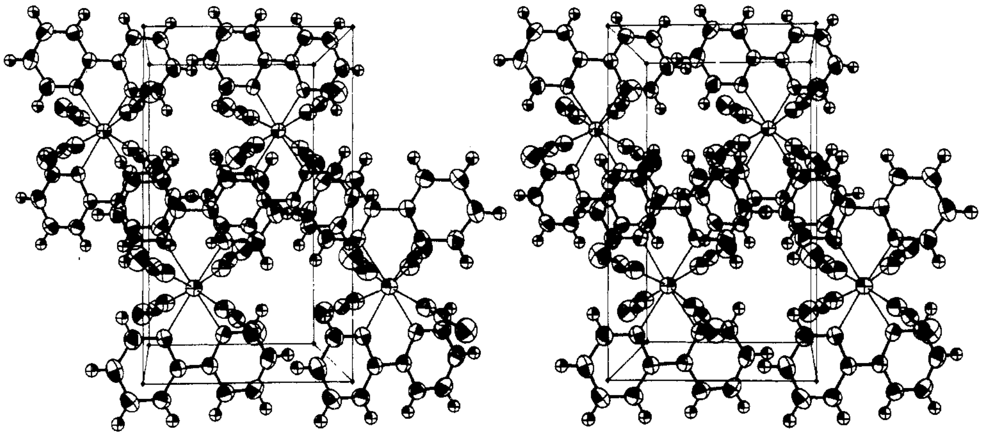


Figure 2. Stereoview of the crystal packing in $Nb(NCS)_4(C_{10}H_8N_2)_2$.

Table VI. Selected Distances (A) in $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $Zr(NCS)_4(C_{10}H_8N_2)_2$

Atoms	Nb value	Zr value	Atoms	Nb value	Zr value
			Bond Distances		
M–N1	2.135 (3)	2.182 (2)	C2–C3	1.391 (4)	1.390 (4)
M–N2	2.318 (3)	2.412 (2)	C3–C4	1.381 (5)	1.384 (4)
N1–C1	1.159 (4)	1.160 (3)	C4–C5	1.375 (6)	1.372 (5)
C1–S1	1.599 (3)	1.590 (3)	C5–C6	1.373 (5)	1.367 (4)
N2–C2	1.353 (4)	1.351 (3)	$C2_a$–$C2_d$	1.463 (6)	1.477 (5)
N2–C6	1.348 (4)	1.350 (4)			
			Nonbonded distances		
N2–C4	2.788 (5)	2.780 (4)	$C3_a$–$C3_d$	2.974 (8)	2.939 (6)
C2–C5	2.740 (5)	2.731 (4)	$N2_a$–$N2_d$	2.672 (5)	2.700 (4)
C3–C6	2.690 (5)	2.701 (4)	N2–C3	2.383 (5)	2.390 (4)
C4–C6	2.368 (6)	2.361 (5)	N1–S1	2.758 (3)	2.750 (2)
			Close Contacts		
S–H3′	3.16 (3)		S–H5′	3.13 (4)	
S–H4′	3.16 (4)		N1–H6	2.38 (3)	2.33 (2)
			C1–H6	2.68 (3)	2.67 (3)

Table VII. Selected Interatomic Angles (deg) for $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $Zr(NCS)_4(C_{10}H_8N_2)_2$

Atoms	Nb value	Zr value	Atoms	Nb value	Zr value
N1a–M–N1b	116.1 (3)	111.0 (2)	M–N2–C2	118.3 (5)	119.1 (4)
N1a–M–N1d	141.6 (2)	143.4 (2)	M–N2–C6	124.0 (5)	123.3 (4)
N1a–M–N1c	77.1 (2)	80.7 (1)	C2–N2–C6	117.8 (6)	117.6 (5)
N2a–M–N2b	119.5 (2)	122.6 (2)	N1–C1–S1	178.8 (3)	179.3 (3)
N2c–M–N2d	70.4 (1)	68.0 (1)	N2–C2–C3	120.6 (6)	121.4 (5)
N2a–M–N2c	147.5 (2)	146.6 (1)	N2a–C2a–C2d	116.6 (7)	116.9 (6)
N1a–M–N2a	77.5 (1)	76.7 (1)			
N1a–M–N2c	77.2 (1)	78.0 (1)	C2–C3–C4	120.8 (7)	119.7 (6)
N1a–M–N2d	139.0 (1)	138.7 (1)	C3–C4–C5	118.1 (8)	118.7 (6)
N1a–M–N2b	71.6 (1)	71.7 (1)	C4–C5–C6	119.0 (7)	119.1 (6)
M–N1–C1	166.5 (3)	163.1 (3)	C5–C6–N2	123.7 (7)	123.5 (6)

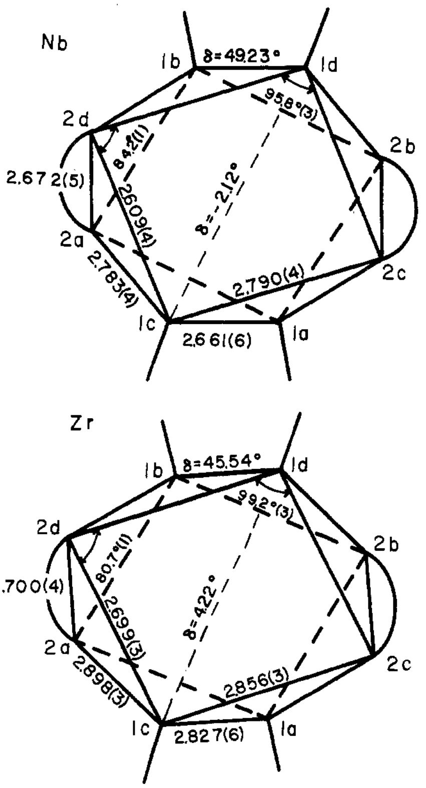


Figure 3. Schematic views of the coordination geometries of $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $Zr(NCS)_4(C_{10}H_8N_2)_2$ with all pertinent distances and angles. δ values given are given for thiocyanates in b sites.

2, while Figure 3 shows the pertinent distances in the coordination polyhedra of both the niobium and zirconium complexes. Bond lengths for both molecules are systematically recorded in Table VI and bond angles are given in Table VII. Several important least-squares planes along with deviations of the atoms from these planes are given in Table VIII for $Nb(NCS)_4(C_{10}H_8N_2)_2$ and in Table IX for $Zr(NCS)_4(C_{10}H_8N_2)_2$.

Discussion

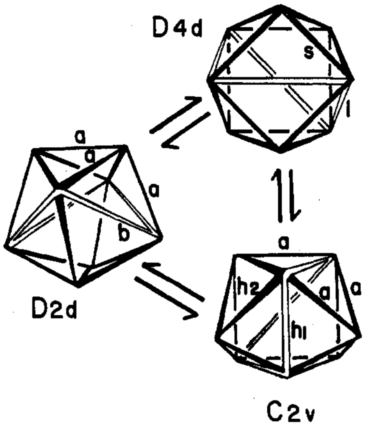
The crystalline compounds, $Nb(NCS)_4(C_{10}H_8N_2)_2$ and $Zr(NCS)_4(C_{10}H_8N_2)_2$, are made up of monomeric eight-coordinate molecules separated by normal van der Waals distances. The two structures are isomorphous, crystallizing in the same space group, *Pnnn*, with the metal atoms at special positions which are the intersection of three twofold axes, thus imparting 222 (D_2) symmetry to each molecule. The metal atom, in each case, is bonded to four nitrogens from thiocyanate groups and four nitrogens belonging to the two bidentate bipyridine groups.

Assignments of coordination polyhedra to eight-coordinate compounds have recently been made by describing the coordination geometry in terms of distortions from a reference polyhedron.[7,8] The reference polyhedron is the D_{2d} dodecahedron, and the two other idealized polyhedra, the D_{4d} square antiprism and the C_{2v} bicapped trigonal prism, are obtained by the appropriate stretching of the dodecahedral b edges. These polyhedral shapes may be distinguished by the dihedral angles, δ (double lines in the figure), defined by the related triangular faces on each polyhedron. Thus, the three most common eight-coordinate polyhedra are interrelated along geometric reaction pathways and a comparison of the dihedral angles should lead to an unambiguous description of the stereochemistry in terms of distortions along these

Table VIII. Least-Squares Planes and Deviations Therefrom for $Nb(NCS)_4(C_{10}H_8N_2)_2$[a]

Atom	Dev, Å	Atom	Dev, Å
(A) Four Coordinated Nitrogens on Square Face			
$1.0000X + 0.0000Y + 0.0000Z = 3.079$			
N1a	−0.018	N1b	−0.018
N2a	0.018	N2b	0.018
(B) Trapezoidal Plane of Idealized Dodecahedron			
$0.7439X - 0.0000Y - 0.6683Z = -0.755$			
N1a	−0.275	N1d	0.275
N2a	0.434	N2d	−0.434
(C) One Pyridyl Ring of Bipyridine			
$0.4723X - 0.0395Y - 0.8806Z = 6.392$			
N2a	−0.022	C4a	−0.010
C2a	0.023	C5a	0.010
C3a	−0.007	C6a	0.005
(D) Other Pyridyl Ring of Bipyridine			
$0.4723X + 0.0395Y - 0.8806Z = 5.458$			
N2d	0.022	C4d	0.010
C2d	−0.023	C5d	−0.010
C3d	0.007	C6d	−0.005
(E) Bipyridine Ring			
$0.4883X + 0.0000Y - 0.8727Z = 5.754$			
N2a	0.003	N2d	−0.003
C2a	−0.011	C2d	0.011
C3a	−0.073	C3d	0.073
C4a	−0.049	C4d	0.049
C5a	0.030	C5d	−0.030
C6a	0.056	C6d	−0.056

[a] Equations describing planes are presented in Cartesian coordinates.



pathways.

Table IX. Least-Squares Planes and Deviations Therefrom for $Zr(NCS)_4(C_{10}H_8N_2)_2$

Atom	Dev, Å	Atom	Dev, Å
(A) Four Coordinated Nitrogens on Square Face			
$1.0000X + 0.0000Y + 0.0000Z = 3.109$			
N1a	0.039	N1b	0.039
N2a	−0.039	N2b	−0.039
(B) Trapezoidal Plane of Idealized Dodecahedron			
$0.7300X + 0.0000Y - 0.6835Z = -0.868$			
N1a	−0.234	N1d	0.234
N2a	0.372	N2d	−0.372
(C) One Pyridyl Ring of Bipyridine			
$0.4841X - 0.0142Y - 0.8749Z = 6.058$			
N2a	−0.017	C4a	−0.009
C2a	0.018	C5a	0.009
C3a	−0.005	C6a	0.004
(D) Other Pyridyl Ring of Bipyridine			
$0.4841X + 0.0142Y - 0.8749Z = 5.772$			
N2d	0.017	C4d	0.009
C2d	−0.018	C5a	−0.009
C3d	0.005	C6d	−0.004
(E) Bipyridine Ring			
$0.4997X + 0.0000Y - 0.8662Z = 5.739$			
N2a	−0.022	N2d	0.022
C2a	−0.014	C2d	0.014
C3a	−0.041	C3d	0.041
C4a	−0.020	C4d	0.020
C5a	0.027	C5d	−0.027
C6a	0.023	C6d	−0.023

[a] Equations describing planes are presented in Cartesian coordinates.

Table X. Symmetry-Independent Shape Parameters for Observed and Theoretical Configurations (deg)

Species	δ angles for bpy in b sites	δ angles for NCS in b sites
$Nb(NCS)_4(bpy)_2$	2.3, 61.4	−2.1, 49.2
Normalized Nb[a]	−3.5, 54.9	3.4, 55.1
$Zr(NCS)_4(bpy)_2$	−5.0, 65.0	4.2, 45.5
Normalized Zr[a]	−12.0, 57.1	11.3, 52.8
Dodecahedron	29.5, 29.5, 29.5, 29.5	
Bicapped trigonal prism	0.0, 21.8, 48.2, 48.2	
Square antiprism	0.0, 0.0, 52.4, 52.4	

[a] These δ values were obtained from a set of coordinates that were generated after the M–N distances were normalized to a single value.

Consider now the arrangement of the ligands in the $M(NCS)_4(C_{10}H_8N_2)_2$ system. If the niobium and zirconium complexes were dodecahedral, there would exist two equally plausible ways of placing the ligands on the idealized polyhedron. Kepert suggested[6] that for compounds of the type MX_4Y_4, where all ligands are not identical, the ligands which form the longer bonds favor the A sites. Thus we would expect the bipyridine nitrogens to occupy the A sites and the thiocyanate nitrogens to occupy the B sites. Kepert has also suggested[34] that for complexes of the type $M(A)_4(B–B)_2$, the choice between the dodecahedral and square-antiprismatic configurations may depend on the ligand "bite" which is defined as the distance between the donor atoms divided by the donor atom to central atom bond length. The bites in the present investigation are 1.119 for the zirconium compound and 1.153 for the niobium compound. The values are less than the ideal value of 1.20 for a square antiprism, which makes it difficult to predict accurately the configuration based upon these considerations. When the bipyridine ligands span the a edges and the thiocyanates occupy the B sites of an idealized D_{2d} dodecahedron, it becomes evident that the H(6)–N(1) and H(6)–C(1) interactions are much too great for dodecahedral symmetry to be retained. Thus the AABB dodecahedral trapezoids are twisted to alleviate the repulsive forces and, in turn, give the observed configuration which retains D_2 symmetry. The other alternative is to have the bipyridine ligands span the b edges. Because of the normalized bipyridine bite discussed earlier, this situation necessitates a contraction of the spanned b edges and a gross extension of the other two b edges. This operation yields two nearly square faces with b edges as diagonals. Of course, a perfect square is not possible because the Nb–N bond distances are not identical. It is apparent that both of the above situations are consistent with the observed configuration and molecular point symmetry and thus shape parameters were calculated for both alternatives.

The symmetry-independent δ angles are tabulated for both observed and idealized configurations in Table X. It is immediately evident that confusion could result due to some of the more unusual values which are observed for these structures. Choice of the bipyridine ligands spanning the b edges leads to one shape parameter of 61.4° for the niobium complex and 65.0° for the zirconium complex which is outside the dodecahedral–square antiprism range, and yet, if the thiocyanate ligands occupy the B sites, then the dihedral angle across the square face in the niobium complex is slightly concave. It was felt, however, that this concave angle could be explained by the differing Nb–N lengths and this supposition was justified when the bond distances were normalized (see Table X). Thus the thiocyanates were chosen to be in the B sites of a D_{2d} dodecahedron and the bipyridine ligands were chosen to span the a edges, these assignments being consistent with Kepert's observations. The appropriate shape parameters for this description of the configuration are given in column 3 of Table X. Comparison of the experimentally observed δ values for both the niobium and zirconium complexes with the idealized hard-sphere polyhedra suggests that both molecules approximate the square-antiprismatic configuration, with the bidentate bipyridine ligands spanning two lateral (l) edges. It appears that the niobium complex actually adopts the antiprismatic structure, this fact being vividly apparent when the δ angles for the normalized complexes are examined. Thus both molecules lie on a geometric reaction pathway between a dodecahedron and square antiprism which, of necessity, retains D_2 symmetry, with the niobium molecule more closely approaching an idealized D_{4d} square antiprism. The larger distortion of the niobium complex from a dodecahedron is probably explained by the smaller M–N bond distances in that complex with a concomitant increase in ligand crowding.

The description of the coordination polyhedron of both complexes as discussed above is substantiated by other relevant criteria. The ϕ angle, calculated as described by Muetterties and Guggenberger[8] (another indicator of distortions in the AABB dodecahedral trapezoid), is 26.8° for the niobium complex and 22.5° for the zirconium complex. The ϕ value for an idealized hard-sphere square antiprism is 24.5°. The ω angle described by Lippard and Russ,[35] the dihedral angle between the dodecahedral trapezoidal planes, is 83.9° for the niobium complex and 86.2° for the zirconium complex. This angle should be 90° for an idealized dodecahedron and 79.4° for an idealized square antiprism. Several complexes, such as $\mathrm{Zr(acac)_4}$[17] and $\mathrm{HPipEu(BA)_4}$[36], have had similar angular values and have been described as antiprisms. Again the observed angles indicate that the niobium complex is distorted more toward the square-antiprismatic structure than is the zirconium complex. Last, it is of interest to examine several least-squares planes which provide qualitative indications of how closely the complexes approach the square-antiprismatic structure. The least-squares planes defining the square faces for these two structures and the deviations of the atoms from these planes indicate virtually planar arrangements for these atoms in both cases. The deviations of the four nitrogens defining the square face were no greater than 0.02 Å in the niobium complex and 0.04 Å in the zirconium complex. Examination of the four nitrogens which define the dodecahedral trapezoidal AABB plane and the deviations of the nitrogens from this plane also point to the niobium complex being more distorted away from a dodecahedron along the geometrical reaction pathway than the zirconium complex. The combination of all of these criteria along with the evidence provided by the shape parameters makes the assignment of a grossly distorted D_{2d} dodecahedron or a D_4 square antiprism with slight distortions rather unambiguous for both complexes.

The arrangement of the bidentate ligands in this structure is extremely rare. Only one $\mathrm{M(A{-}A)_4}$ type compound, i.e., $\mathrm{Nb[(\mathit{t}\text{-}C_4H_9CO)_2CH]_4}$,[9] has the bidentate groups bridging the square faces of the antiprism and no $\mathrm{M(A{-}A)_2B_4}$ systems with this unique ligand arrangement have been observed. It was of interest to investigate the effect of the polyhedral shape and this unique ligand "wrap" on the usual coordinating properties of the bipyridine ring. An examination of the least-squares planes for the two pyridyl portions of the bipyridine (planes C and D) and the entire bipyridine ligand (plane E) indicates that the two pyridyl rings are twisted slightly with respect to each other and in relation to the least-squares plane of the bipyridine. This slight distortion occurs to a greater extent in the niobium complex than in the zirconium complex. The dihedral angle between the planes of the two pyridyl rings is 4.5° for the niobium complex and 1.6° for the zirconium complex, while the angles that the pyridyl ring makes with the bipyridine ring are 2.5 and 1.3°, respectively. This slight distortion is probably necessary to alleviate further the H(6)–C(1) and H(6)–N(1) contacts. The ligand bite distances of 2.672 Å in the niobium complex and 2.700 Å in the zirconium complex are quite similar to those found in other complexes containing bipyridine. As shown in Tables VI and VII, all bond distances and bond angles within the bipyridine rings of both complexes, along with all important nonbonded distances, are consistent with values reported for this ligand in other structures. Thus the behavior of bipyridine as a ligand would appear to be quite normal, with slight distortions necessary in order to help to alleviate ligand crowding.

The inability of the niobium complex to achieve an undistorted square-antiprismatic structure is due to the differing Nb–N bond distances. The Nb–N1 bond distance is 2.135 Å and the Nb–N2 distance is 2.318 Å. These values seem to be in reasonable agreement with other literature values, but it must be noted that niobium–nitrogen distances are indeed scarce in the literature. The observed niobium–nitrogen distances in $\mathrm{NbCl_3[NMeC(:S)Me]_2}$[37] are 2.23 and 2.18 Å, while the niobium–nitrogen single-bond distance is 2.38 Å in $\mathrm{(\pi\text{-}C_5H_5)(PH_3)Nb[HCPh(CPh)_3C({=}NH)CH_3]}$.[38] Perhaps the most significant structures for comparison are $\mathrm{(Ph_4As\text{-}([NbO(NCS)_5]}$,[39] where the niobium–nitrogen distances range from 2.03 to 2.27 Å depending on the position of the thiocyanate ligand, and $\mathrm{Nb[(OC_2H_5)(O)Cl_2(C_{10}H_8N_2)]}$,[39] which has niobium–nitrogen single-bond distances of 2.32 and 2.35 Å. Thus it seems that the niobium–nitrogen distances are quite in line with previously reported values. In fact, it could be argued that these niobium–nitrogen distances are the most representative values determined for eight-coordinate complexes, to date, because of the relative simplicity of the structure.

The fact that the zirconium complex is not as far along on the reaction pathway as the niobium complex is probably due to the longer metal–nitrogen bond distances in this molecule, which reduces ligand crowding. The Zr–N1 bond distance is 2.182 Å and the Zr–N2 distance is 2.412 Å. As was the case with the niobium complex, there are not many zirconium complexes containing coordinated nitrogen available for comparison. The zirconium–nitrogen single-bond distance in the complex anion $\mathrm{Zr[N(CH_2COO)_3]_2^{2-}}$[40] is 2.44 Å. The eight-coordinate Schiff base compound $\mathrm{Zr(OC_6H_4CH{:}NEt)_4}$[41] has a zirconium–nitrogen distance of 2.54 Å, while $\mathrm{Zr[C_2H_4N_2(CH_2COO)_4]\cdot 4H_2O}$[42] has a zirconium–nitrogen distance of 2.41 Å. These distances agree well with the Zr–N2 distance but are somewhat longer than the Zr–N1 distance which is understandable considering the ligands involved. Again, the observed zirconium–nitrogen bond distances can be considered to be more representative because of the simplicity of the structure. The 0.05-Å increase in the metal–thiocyanate nitrogen bond length, on going from niobium to zirconium, can be attributed solely to the increase in ionic size upon going from Nb(IV) to Zr(IV) (an approximate increase of 0.05 Å). However, the reasons for the 0.1-Å increase in the metal–bipyridine nitrogen bond length on going from niobium to zirconium are somewhat obscure. Whether this observation can be explained completely by the larger ionic size of Zr(IV) vs. Nb(IV) or whether the d electron (in the niobium complex) is significant in decreasing the metal–ligand bond length is open to discussion at this time.

The important distances and angles of the coordination polyhedra are shown on schematic drawings of the complexes in Figure 3. The nonbonded nitrogen–nitrogen distances are larger in the zirconium complex, consistent with less ligand crowding, than in the niobium complex. An examination of the angles and distances in the quasi-square faces in both complexes shows that the four nitrogens defining this face are more nearly square in the niobium complex as expected.

Also of considerable interest is the bonding in the thiocyanate ligand. The carbon–nitrogen bond distance is 1.159 Å in the niobium complex and 1.160 Å in the zirconium complex. The carbon–sulfur distances are 1.599 and 1.590 Å, respectively. These values agree well with distances reported for other structures containing thiocyanate and also the theoretical values for a $C\equiv N$ bond (1.218 Å) and a C—S bond (1.557 Å) as given by Pauling.[43] These values coupled with a M–N–C bond angle near 180° would seem to indicate that the bonding within the ligand can be described as predominantly sp hybridization, a conclusion drawn by many authors.[44] However, the Nb–N–C bond angle is 166.5° and the Zr–N–C bond angle is 163.1°, which are significant distortions from the theoretical value. This observed nonlinearity of the M–N–C bond angle is readily explained by packing conditions in the crystal. The closest approach between $Nb(NCS)_4(C_{10}H_8N_2)_2$ molecules, as shown in Figure 2, would appear to be between the bipyridine hydrogens (H3, H4, H5) and the sulfur of a thiocyanate group of a neighboring molecule. In the crystal structure each molecule is directly above a molecule in the next unit cell (Nb–Nb distance is 7.70 Å). The van der Waals radii of sulfur and hydrogen, as reported by Pauling,[43] are 1.85 and 1.1 Å, respectively. The close contact values are all approximately 3.15 Å, and it is certain that this value is closer to 3.05 Å because the carbon–hydrogen distances are actually longer than observed. It would seem that it is necessary for the thiocyanate group to be bent in order to balance the attractive forces between the molecules, and this bend occurs away from the plane of the approaching bipyridine ring. Thus the geometry of the thiocyanate ligand appears to be a consequence of crystal packing and not to be due to a great extent to interligand repulsions.

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Registry No. $Nb(NCS)_4(C_{10}H_8N_2)_2$, 38669-93-1; $Zr(NCS)_4(C_{10}H_8N_2)_2$, 38356-68-2.

Supplementary Material Available: Listings of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

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