filled, in agreement with the almost nonmagnetic behavior of the Rh atoms. With the inclusion of the Er atoms, the Fermi level cuts through many bands. Thus, the metallic conductivity can be rationalized.

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Supplementary Material Available: Listings of the crystallographic data and the anisotropic thermal parameters for the metal atoms of $Er_8Rh_5C_{12}$ (1 page); a structure factor table (11 pages). Ordering information is given on any current masthead page.

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Ru(2,2′-bpy)$_2$(NCS)$_2$·X [X = CH_3CN, $(CH_3)_2SO$] and Related Compounds: Crystal Structure, VTFTIR, and NMR Study

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The crystal structures of Ru(bpy)$_2$(NCS)$_2$, solvated with CH_3CN and $(CH_3)_2SO$, have been determined. Ru($C_{10}H_8N_2$)$_2$(NCS)$_2$·CH_3CN crystallizes in the monoclinic space group *C*2/*c* with a = 10.230 (2) Å, b = 15.209 (3) Å, c = 16.186 (2) Å, β = 105.19 (1)°, $Z = 4$, and R_F (R_{wF}) = 0.037 (0.046) for 1023 reflections with $F_o^2 > 3\sigma(F_o^2)$; Ru($C_{10}H_8N_2$)$_2$(NCS)$_2$·$(CH_3)_2SO$ crystallizes in the triclinic space group $P\bar{1}$ with a = 12.402 (2) Å, b = 12.732 (2) Å, c = 8.853 (1) Å, α = 105.70 (3)°, β = 103.06 (2)°, γ = 83.65 (3)°, $Z = 2$, and R_F (R_{wF}) = 0.053 (0.068) for 3517 reflections with $F_o^2 > 3\sigma(F_o^2)$. In both complexes, the isothiocyanate ligands are cis. The CN absorbance in the IR spectra of the desolvated complex, as well as in the spectra of mulls of the DMSO-solvated material, has been determined and compared to those in the IR spectra of related cis and trans octahedral complexes of bis(isothiocyanate) species. The ^{13}C NMR spectra in DMSO-d_6 show the expected 11 resonances associated with the cis configuration observed in the X-ray determinations. The implications of the spectroscopic signatures of these complexes in relation to their structures in the solid state and the extent to which these signatures are diagnostic with respect to the symmetry properties of these complexes are discussed.

Introduction

The chemistry of Ru(II) has received a great deal of attention in recent years, largely due to the richness of available oxidation states, large variability of ligand lability, and ease of coordination sphere modification available in ruthenium complexes.[1] Moreover, because of the great interest in determining the rate of electron transfer in biological systems, ruthenium complexes have been used as models for studying such processes on a rapid (nanosecond) time scale in a variety of chemical environments.[2-6] In this latter context, variable-temperature Fourier transform infrared spectroscopy (VTFTIR) has proven to be a potentially fruitful method to examine the rate of electron transfer in mixed-valence compounds. This approach is predicated on the assumption that each metal center can be ligated with an appropriate "reporter" ligand, the IR signature of which will reflect the oxidation state and molecular level architecture of the metal center to which it is bonded. As has been discussed[7] previously for a variety of inorganic and organometallic compounds, the thiocyanate and selenocyanate ligands can play the role of such a reporter group, and the detailed IR spectra of a large number of such compounds have been reported. Despite the fact that Ru(II) thiocyanates have been known[8,9] for a number of years, no detailed structural studies, based on single-crystal X-ray diffraction data, have been reported, and the structural details of such compounds have been inferred indirectly from other (largely vibrational spectroscopic) data. In this context, a detailed VTFTIR study of rigorously desolvated Ru(2,2′-bpy)$_2$(NCS) has recently been reported.[10] The observation of a single, symmetric absorbance in the CN stretching region, as well as an absorbance in the Raman spectrum at nearly the same frequency, has been interpreted as evidence for a trans configuration of the two pseudohalide groups, in contrast to the cis configurations that have been assigned to the corresponding bis(chloro)[11] and bis(cyano) complexes.[12,13] In the course of this IR study, it was observed that well-formed single crystals of the title compound could be recovered from CH_3CN and DMSO solutions. It has also proven feasible to examine the ^1H and ^{13}C NMR spectra of the title compound in DMSO-d_6, as well as the infrared spectra of these solvated crystals in the presence of mother liquor. Finally, it has also proven possible to study the systematics of a number of related model compounds containing the SCN^- ligand. The details of these investigations are summarized in the present paper.

Experimental Section

(a) Preparation of Ru(2,2′-bpy)$_2$(NCS)$_2$·CH_3CN (1) and Ru(2,2′-bpy)$_2$(NCS)$_2$·$(CH_3)_2SO$ (2). The parent aquo-solvated compound reported in this study was prepared by literature methods and characterized

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(1) Taube, H. *Comments Inorg. Chem.* **1981**, *1*, 17.
(2) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.
(3) Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443.
(4) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
(5) Mayo, S. L.; Ellis, W. R., Jr.; Crutchley, R. J.; Gray, H. B. *Science* **1986**, *233*, 948.
(6) Plitzko, K.-D.; Boekelheide, V. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 700.
(7) Herber, R. H. *Rev. Silicon, Germanium, Tin Lead Compd.* **1986**, *9*, 113.
(8) For a detailed review of the literature through 1983, see: Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier, New York, 1984; and references therein.
(9) Brandt, W. W.; Dwyer, F. P.; Gyarfas, E. C. *Chem. Rev.* **1954**, *54*, 959.
(10) Herber, R. H.; Nan, G. *Inorg. Chem.* **1988**, *27*, 2644.
(11) Bosnich, B.; Dwyer, F. P. *Aust. J. Chem.* **1966**, *19*, 2229. Goodwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 471.
(12) Demas, J. N.; Turner, T. F.; Crosby, G. A. *Inorg. Chem.* **1969**, *8*, 674.
(13) Schilt, A. A. *Inorg. Chem.* **1964**, *3*, 1323.

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Table I. Crystal and Refinement Data for Ru(2,2′-bpy)$_2$(NCS)$_2$·X

	X = CH$_3$CN (**1**)	X = (CH$_3$)$_2$SO (**2**)
formula	$RuS_2N_7C_{24}H_{19}$	$RuS_3N_6C_{24}H_{22}O$
fw	570.66	607.74
a, Å	10.230 (2)	12.402 (2)
b, Å	15.209 (3)	12.732 (2)
c, Å	16.186 (2)	8.853 (1)
α, deg	90	105.70 (3)
β, deg	105.19 (1)	103.06 (2)
γ, deg	90	83.65 (3)
V, Å^3	2430 (1)	1309 (1)
space group	*C*2/*c*	*P*$\bar{1}$
Z	4	2
d_{calcd}, g cm^{-3}	1.560	1.54
d_{obsd}, g cm^{-3}	1.55 (1)	
radiation (λ, Å)	graphite-monochromated Mo Kα (0.71073)	
linear abs coeff, cm^{-1}	8.2	8.4
temp, K	295 (1)	294 (1)
final R_F, R_{wF}[a]	0.037, 0.046	0.053, 0.068

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

by elemental analysis [Anal. Found (calcd) for $RuC_{22}H_{16}N_6S_2 \cdot H_2O$: C, 48.09 (48.08); H, 2.95 (3.67); N, 15.10 (15.29); S, 11.94 (11.67)], as well as IR and NMR spectroscopy (vide infra). The Ru(bpy)$_2$(NCS)$_2$ complex was obtained by using both a photochemical[14,15] and a "dark" synthetic procedure,[16] and the solvated forms were obtained by slow evaporation of solutions of these synthetic products from CH$_3$CN or DMSO (DMSO-d_6) to form Ru(bpy)$_2$(NCS)$_2$·CH$_3$CN (**1**) or Ru(bpy)$_2$(NCS)$_2$·(CH$_3$)$_2$SO (**2**), respectively. Crystals of **1** were obtained by slow solvent evaporation, which afforded rectangular crystals, most of which showed numerous imperfections running parallel to the long crystal axis. Smaller crystals were also formed without these striations and extinguished well under crossed-polarizer observation. Extensive microscopic examination was used to select crystals that exhibited no obvious striations. These were stable when studied optically under mineral oil. Finally, a crystal of **1** was selected whose diffraction peaks were sharp enough to permit a good data set to be obtained. Crystals of **2** were obtained by slow evaporation of the solution of the parent complex in DMSO.

(b) VTFTIR Spectroscopy. Vibrational spectra in the midrange (4800–400 cm^{-1}) were acquired in the temperature range 78 < *T* < 300 K by using the arrangement described earlier.[17-19] Both KBr pellets (less than ~0.5% by weight due to the high oscillator strength of the CN stretch) and mulls in Nujol, Kel-F grease, and DMSO, as well as solution spectra in CH$_3$CN and DMSO, were examined in an attempt to correlate the band profile with the solid-state and solution environments of the chromophore.

(c) Nuclear Magnetic Resonance Spectroscopy. Saturated solutions of **2** in DMSO-d_6 were filtered, ^{1}H and ^{13}C spectra were recorded (256 and 30 000 scans, respectively) by using a Varian XL-200 multinuclear probe spectrometer, and a ^{13}C spectrum (43 000 scans) was recorded by using a Varian XL-400 instrument. The solubility limitations in acetonitrile (vide infra) precluded carrying out the same measurements on **1**.

(d) X-ray Diffraction Studies. A purple, tabular crystal of **1** was removed from the mother liquor and blotted dry. Following microscopic examination while it was covered with mineral oil, the crystal was mounted with silicone grease in a glass capillary, well removed from a small amount of mother liquor. Diffraction measurements on **1** were made with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation. The Enraf-Nonius Structure Determination Package[20] was used for data collection, data processing, and structure solution. Diffractometer examination of the reciprocal lattice revealed a monoclinic system, and systematic absences were consistent with space group *Cc* or *C*2/*c*. Successful solution and refinement of the structure confirmed *C*2/*c* as the correct space group. Crystal data and additional details regarding data collection and refinement are presented in Table I. Intensity data were collected and corrected for decay, absorption (empirical), and Lp effects.

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**

	x	*y*	*z*	B_{eq},[a] Å^2
Ru	0.000	0.04842 (5)	0.250	3.19 (2)
S	0.1580 (3)	0.2850 (2)	0.1039 (1)	7.91 (7)
N(1)	0.0883 (5)	0.1450 (3)	0.1941 (3)	4.0 (1)
N(2)	0.0772 (5)	−0.0459 (3)	0.1864 (3)	3.5 (1)
N(3)	−0.1488 (5)	0.0402 (3)	0.1373 (3)	3.6 (1)
C(1)	0.1144 (7)	0.2027 (4)	0.1581 (4)	4.3 (2)
C(2)	0.1990 (7)	−0.0837 (4)	0.2146 (4)	4.4 (2)
C(3)	0.2459 (7)	−0.1481 (5)	0.1675 (5)	5.3 (2)
C(4)	0.1632 (8)	−0.1741 (5)	0.0902 (5)	5.8 (2)
C(5)	0.0387 (8)	−0.1360 (5)	0.0614 (4)	5.1 (2)
C(6)	−0.0032 (7)	−0.0699 (4)	0.1095 (4)	3.8 (2)
C(7)	−0.1295 (6)	−0.0215 (4)	0.0818 (4)	3.7 (2)
C(8)	−0.2236 (7)	−0.0345 (5)	0.0030 (4)	5.0 (2)
C(9)	−0.3366 (7)	0.0181 (5)	−0.0179 (5)	6.0 (2)
C(10)	−0.3568 (7)	0.0828 (5)	0.0387 (5)	5.9 (2)
C(11)	−0.2612 (7)	0.0904 (5)	0.1157 (4)	4.4 (2)
N(4)	0.000	0.5428 (9)	0.250	10.9 (4)
C(12)	0.000	0.618 (1)	0.250	7.4 (4)
C(13)	0.000	0.7128 (8)	0.250	9.2 (4)

[a] Anisotropically refined atom thermal parameters are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

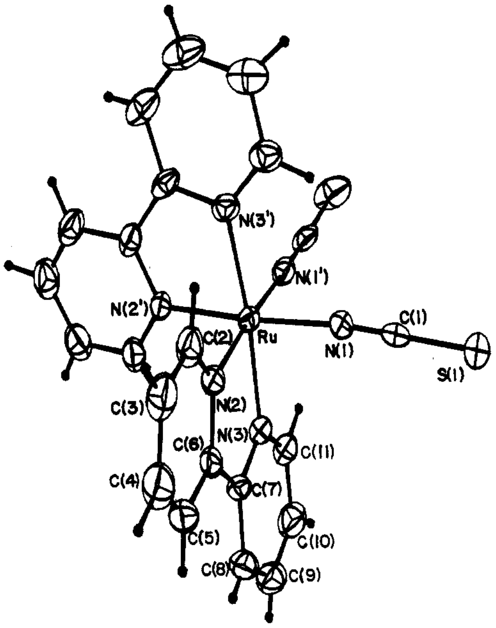

Figure 1. ORTEP diagram of Ru(2,2′-bpy)$_2$(NCS)$_2$]·CH$_3$CN. The solvate molecule has been omitted for clarity.

The structure of **1** was solved by direct methods[21] and refined on *F* with full-matrix least-squares techniques. An *E* map, based on 222 phases (|*E*| > 1.20), from the starting set having the highest combined figure-of-merit revealed coordinates for Ru, the NCS ligands, and several atoms from the bipyridyl ligands. The remaining non-H atoms, including those of the acetonitrile solvate, were located from successive difference maps. At this point, it was noted that both the Ru atom and the acetonitrile solvate were located on 2-fold axes in *C*2/*c*, implying a disorder for the methyl group H atoms. Following anisotropic refinement, all bipyridyl H atoms were located on a difference map; solvate H atoms were not located. Hydrogen atom temperature factors were set according to $B_H = 1.3B_N$, where N is the atom bonded to H. The H atom parameters were not refined. Several cycles of refinement with all non-H atoms anisotropic led to convergence with $R_F = 0.037$, $R_{wF} = 0.046$, and GOF = 1.50. A final difference map showed a general background of about

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(14) Durham, B.; Walsh, J. L.; Carter, C. L.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 860.
(15) Hoggard, P. E.; Porter, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 1457.
(16) Wajda, S.; Rachlewicz, K. *Inorg. Chim. Acta* **1978**, *31*, 35.
(17) Casson, L. M.; Herber, R. H. *Rev. Sci. Instrum.* **1985**, *56*, 1593.
(18) Herber, R. H.; Casson, L. M. *Inorg. Chem.* **1986**, *25*, 847.
(19) Herber, R. H. *Inorg. Chem.* **1987**, *26*, 173.
(20) Frenz, B. A. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, Holland, 1983.
(21) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "MULTAN 82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and University of Louvain, Belgium, 1982.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for **1**

Ru–N(1)	2.055 (5)	C(3)–C(4)	1.371 (9)
Ru–N(2)	2.041 (4)	C(4)–C(5)	1.365 (9)
Ru–N(3)	2.051 (4)	C(5)–C(6)	1.406 (8)
S–C(1)	1.654 (7)	C(6)–C(7)	1.452 (8)
N(1)–C(1)	1.124 (7)	C(7)–C(8)	1.397 (8)
N(2)–C(2)	1.340 (8)	C(8)–C(9)	1.374 (9)
N(2)–C(6)	1.351 (7)	C(9)–C(10)	1.40 (2)
N(3)–C(7)	1.349 (7)	C(10)–C(11)	1.373 (8)
N(3)–C(11)	1.348 (7)	N(4)–C(12)^a	1.14 (2)
C(2)–C(3)	1.401 (8)	C(12)–C(13)^a	1.44 (2)
N(1)–Ru–N(1′)	88.7 (3)	S–C(1)–N(1)	177.5 (6)
N(1)–Ru–N(2)	90.4 (2)	N(2)–C(2)–C(3)	122.3 (6)
N(1)–Ru–N(2′)	175.8 (2)	C(2)–C(3)–C(4)	118.8 (6)
N(1)–Ru–N(3′)	97.2 (2)	C(3)–(4)–C(5)	119.1 (6)
N(1)–Ru–N(3)	87.8 (2)	C(4)–C(5)–C(6)	120.5 (6)
N(2)–Ru–N(2′)	90.7 (2)	N(2)–C(6)–C(5)	120.2 (6)
N(2)–Ru–N(3′)	96.4 (2)	N(2)–C(6)–C(7)	115.1 (5)
N(2)–Ru–N(3)	78.7 (2)	C(5)–C(6)–C(7)	124.6 (6)
N(3)–Ru–N(3′)	173.0 (3)	N(3)–C(7)–C(6)	114.9 (5)
Ru–N(1)–C(1)	168.2 (5)	N(3)–C(7)–C(8)	121.4 (6)
Ru–N(2)–C(2)	125.3 (4)	C(6)–C(7)–C(8)	123.7 (6)
Ru–N(2)–C(6)	115.6 (4)	C(7)–C(8)–C(9)	118.5 (6)
C(2)–N(2)–C(6)	119.1 (6)	C(8)–C(9)–C(10)	120.5 (7)
Ru–N(3)–C(7)	115.5 (4)	C(9)–C(10)–C(11)	117.5 (6)
Ru–N(3)–C(11)	125.5 (5)	N(3)–C(11)–C(10)	123.1 (6)
C(7)–N(3)–C(11)	119.0 (5)	N(4)–C(12)–C(13)	180^a

^{a}Atoms N(4) and C(13) comprise the acetonitrile solvate framework. This group is situated on a crystallographic 2-fold axis.

±0.3 e/Å^3. The largest peak, 0.68 e/Å^3, was located 1.12 Å from Ru. Final atomic parameters are listed in Table II, while a view of the complex, showing the atom-numbering scheme, is given in Figure 1. The single molecule shown has the Λ conformation, but Δ and Λ conformations must be present in equal numbers in the unit cell of this centrosymmetric space group. Lists of anisotropic thermal parameters, H atom parameters, and observed and calculated structure factors are available (supplementary material).

Data were collected for compound **2** on a Philips PW1100 diffractometer. Crystallographic data and other pertinent information are given in Table I. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were located by using the results of the SHELXS-86 direct-method analysis.[22a] The structure was refined[22b] in space group $P\bar{1}$ to convergence. All the hydrogen atoms were located from the difference Fourier map, and they were included in the final refinement cycles by using the riding model with $U = 0.05$ Å^2. Anisotropic thermal parameters were used for all non-hydrogen atoms. The structure and dimensions of complex **2** are very similar to those found for **1**. Therefore, all positional and thermal parameters and the bond distances and angles are included in the supplementary material, along with the observed and calculated structure factors.

Results and Discussion

(a) Description of the Structure. The structure of **1** consists of neutral *cis*-$Ru^{II}(bpy)_2(NCS)_2$ molecules separated by acetonitrile solvate molecules. The shortest contacts between these species [C(2)···N(4^a) = 3.549 (9) Å, C(3)···C(13^b) = 3.786 (9) Å, where a and b refer to appropriate symmetry-transformed coordinates] suggest no intermolecular bonding stronger than that arising from van der Waals forces.

In **1**, both the $Ru^{II}(bpy)_2(NCS)_2$ and the non-hydrogen portion of the CH_3CN molecules utilize the 2-fold axis located at 0, *y*, $^1/_4$ in space group $C2/c$, and both have C_2 point symmetry. All of the acetonitrile non-H atoms lie on this axis, as does the Ru atom. Six N atoms, four from the bpy and two from the NCS ligands, coordinate Ru in the expected distorted-octahedral fashion. The trans N–Ru–N angles [173.0 (3), 175.8 (2)°; Table III] deviate only slightly from the ideal value of 180°. Corresponding cis angles show similar small (<7°) deviations from 90°, except for N(2)–Ru–N(3), whose smaller value [78.7 (2)°] is attributed to the limited bite of the bidentate bpy ligand. The three unique Ru–N distances are equivalent to each other to ±0.01 Å. Statistically, however, Ru–N(2), which is trans to the isothiocyanate N atom, is marginally shorter than the other two Ru–N distances.

In the present structure, the bpy ligands are approximately planar; atomic position deviations from the least-squares plane are all less than 0.09 Å. These deviations vary systematically along the length of the ligand and indicate a bowed conformation. In *trans*-$(bpy)_2$ octahedral complexes, the bpy ligands are necessarily distorted owing to steric crowding of the α-hydrogen atoms and typically show larger deviations from planarity, with bowed or twisted conformations.[23]

Each pyridine subunit [N(2), C(2)–C(6) and N(3), C(7)–C(11)] is planar to ±0.015 Å (largest deviation is 0.014 Å), and the dihedral angle between these planes [6 (2)°] gives an estimate of the degree of bowing. The two bpy ligands are nearly perpendicular, as indicated by the dihedral angle between their least-squares planes, 86.49 (7)°. Bond distances within the bipyridyl ligand compare favorably with those found for the free ligand[24] and for other bis(bipyridyl)ruthenium(II) complexes.[25,26] The geometry of the thiocyanate ligand is also typical of that found in other structures without Ru.[27]

The Ru–isothiocyanate bond angle [168.2 (5)°] is near the high end of the range observed[28] for metal–thiocyanate angles (ca. 130–180°) in systems where the pseudohalide is N-bonded to the metal. Larger angles are expected[28] if the metal can donate d_π electrons to the π-accepting isothiocyanate ligand, as is the case with Ru(II).

The structures of **1** and **2** are most conveniently compared with those containing cis-bis $(bpy)_2Ru^{II}L_2$ species. Structural data for such complexes with L = NCS, $NCCH_3$,[25] and Cl[29] are given in Table IV, from which it is seen that the geometries of the three species are similar, although there are some differences. For example, there are small, possibly significant differences in the Ru–N distances, which may be related to the π-acceptor ability of L.[29] A more striking difference is in the dihedral angles between the bpy planes in **1** and **3**: 86.49 (7)° in **1** and 72.5 (1)° in **3**. For an octahedron, the value would be 90°, and the significantly smaller value in **3** implies greater distortion from O_h geometry. In **3**, the bpy ligands are pushed back from the ligands L toward the (pseudo) 2-fold axis to a greater extent than in **1**. The N(trans)–Ru–N(trans′) angle, which is reduced from 90.7(2)° in **1** to 86.2 (2)° in **3**, is consistent with this interpretation.

In **1**, the shortest intermolecular contacts [e.g.: C(4)···C(9′) = 3.352 (9) Å; C(5)···C(8′) = 3.524 (8) Å] are between atoms of the bpy groups such that the pyridine rings of the bowed ligands participate in plane–plane stacking arrangements reminiscent of that observed[29] for **4**.

(b) Infrared Spectroscopy. As noted in the earlier study,[10] the CN stretching region of the IR spectra of the rigorously desolvated ruthenium(II) bis(isothiocyanate) complex evidences a single, symmetric, broad (full width at half-maximum of ~29 cm^{-1}) absorbance located at 2100 cm^{-1} at 300 K. This value is only in modest agreement with those reported by Wajda and Rachlewicz[16] (2095 cm^{-1} in KBr pellets and Nujol mulls and 2125 cm^{-1} in dimethylformamide solution) but has been carefully examined both at room temperature and in the range $78 < T < 300$ K in both KBr and Kel-F grease mull spectra. The Raman spectra show an absorbance at 2104 cm^{-1}, which has been assigned to the symmetric stretch of the pseudohalide moiety. When Ru(2,2′-

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(22) (a) Sheldrick, G. M. *Crystallographic Computing 3*; Oxford University Press: Oxford, England, 1985; pp 175–189. (b) All crystallographic computing of the structure of **2** was done on a CYBER 855 computer at The Hebrew University of Jerusalem, using the SHELX 77 structure determination package.

(23) Cordes, A. W.; Durham, B.; Swepston, P. N.; Pennington, W. T.; Condren, S. M.; Jensen, R.; Walsh, J. L. *J. Coord. Chem.* **1982**, *11*, 251.

(24) Merritt, L. L., Jr.; Schroeder, E. D. *Acta Crystallogr.* **1956**, *9*, 801.

(25) Heeg, M. J.; Kroener, R.; Deutsch, E. *Acta Crystallogr.* **1985**, *C41*, 684.

(26) Durham, B.; Wilson, S. R.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 600.

(27) Long, G. J.; Galeazzi, G.; Russo, U.; Valle, G.; Calogero, S. *Inorg. Chem.* **1983**, *22*, 507.

(28) Drew, M. G. B.; bin-Othman, A. H.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1394.

(29) Eggleston, D. S.; Goldsby, K. A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 4573.

Table IV. Structural Comparisons (Å, deg) for *cis*-$(bpy)_2Ru^{II}L_2$ Complexes

	L = NCS[a] (1)	L = NCS[a] (2)	L = $NCCH_3$[b] (3)	L = Cl[c] (4)
Ru-N(L)[d]	2.055 (5)	2.052 (6), 2.059 (5)	2.033 (7), 2.033 (6)	2.426 (1)
Ru-N(trans)[d]	2.041 (4)	2.025 (5), 2.039 (5)	2.040 (5), 2.045 (6)	2.013 (2)
Ru-N(cis)[d]	2.051 (4)	2.055 (5), 2.059 (6)	2.063 (5), 2.067 (6)	2.054 (2)
N(L)-Ru-N(L′)	88.7 (3)	91.3 (2)	87.8 (3)	89.2 (1)
N(trans)-Ru-N(cis)	78.7 (2)	79.1 (2), 79.3 (3)	78.7 (2), 79.4 (2)	79.10 (9)
N(trans)-Ru-N(trans′)	90.7 (2)	91.9 (2)	86.2 (2)	91.6 (1)
N(cis)-Ru-N(cis′)	173.0 (3)	175.0 (2)	172.5 (2)	174.2 (1)
bpy/bpy′[e]	86.49 (7)	84.9 (1)	72.5 (1)	*f*
py/py′[g]	6 (2)	4 (1), 5 (2)	*f*	1.3

[a] This work. [b] Reference 25. [c] Reference 29. [d] N(L) is the nitrogen or chlorine atom in ligand L; N(trans) and N(cis) refer to the ligand atoms trans or cis to N(L), respectively. [e] Dihedral angle between the least-squares planes of the bipyridyl groups. [f] Not reported. [g] Dihedral angle between pyridine planes of the bipyridine ligand.

$bpy)_2(NCS)_2$ is recrystallized from DMSO, large rectangular platelets can be isolated from the solution. When these are separated by centrifugation and washed with cold DMSO, and the wet crystals are mulled with a drop of DMSO and examined between KBr plates at 300 K, the IR band due to the CN stretch shows an asymmetry with a shoulder located at ~2107 cm^{-1}. This asymmetry is (presumably) due to the incorporation of one molecule of DMSO per metal atom in the structure. The infrared spectral regions associated with characteristic DMSO absorbances (2990, 2875, 1435, 1405, and 662 cm^{-1} inter alia) do not show any new bands that can be associated with the DMSO bound in the crystal structure. One possible explanation for this observation is that the solvate molecule–metal complex interaction is sufficiently weak that no pronounced IR shifts can be observed. (It should be noted that the intermolecular contacts in **2** extracted from the X-ray diffraction data show no DMSO–$Ru[(bpy)_2(NCS)_2]$ distances shorter than those expected from van der Waals contact.) With respect to the IR data, it is appropriate to note that even in cases where DMSO is directly bonded to Ru(II), as shown by a single-crystal diffraction study[30] of $(NH_3)_5Ru(DMSO)^{2+}$, in which the DMSO moiety is S-bonded (2.188 (3) Å) to the metal center, the frequency of the S–O stretch remains essentially unshifted from the value observed for neat DMSO in nitromethane (1045 cm^{-1}), despite the more common observation that this band is blue-shifted on S-coordination and red-shifted on O-coordination. In addition, the large excess of nonbound DMSO over that incorporated in the crystal structure may make the latter difficult to resolve from the data. On the other hand, a possible dipole–dipole interaction between the solvate molecule and one (or both) of the NCS^- ligands may account for the significant broadening of the CN stretch. In the homologous Fe(II) complex, which is known[31] to adopt the cis configuration, and in which, as expected, two CN stretches are observed[19] in the IR spectra, the characteristic full width at half-maximum is only 12–15 cm^{-1} under identical conditions.

The observation of a single (albeit broad) CN stretch in IR spectra of **1** and **2**, as well as in that of the desolvated Ru compound, has long been a puzzle in the context of assigning a geometry to the two pseudohalide ligands. For a variety of other well-characterized thiocyanate complexes (e.g., Fe: $Fe(bpy)_2(NCS)_2$, $Fe(phen)_2(NCS)_2$), as well as the related bis(cyano) complex $Ru(bpy)_2(CN)_2$,[12] which are known to have a cis O_h configuration, two well-resolved CN stretches are observed in the IR spectra, usually with band center separations of 6–15 cm^{-1}. Per contra, related complexes (e.g. $M(py)_4(NCS)_2$, where M = Mn, Fe, Co, Ni, and Cu), which are known to have the two NCS^- ligands in trans positions,[32] give rise to a single CN stretch in their IR[33] spectra, as does the complex *trans*-$Pt(py)_2(SCN)_2$ (py = pyridine).[34] The crystal structure of the trans isomer of the latter complex has been reported,[35] but to the best of our knowledge, that of the cis isomer has so far not been examined by X-ray crystallographic methods. In contrast, the complex Pt(phen)-$(SCN)_2$ (phen = 1,10-phenanthroline), which can exist only in the cis configuration, shows two well-resolved IR bands in the CN stretching region, as expected. A systematic infrared study of some of these complexes has been reported by Thornton et al.[33,36] It is interesting to note, in connection with the spectra of the trans complexes, that the symmetric CN stretch, which is forbidden in the IR spectra but allowed in the Raman spectra, is observed at a frequency that is within 1–2 wavenumbers of the asymmetric stretch frequency seen in the IR spectrum. For the Mn, Co, and Ni complexes of $M(py)_4(NCS)_2$, the room-temperature IR and Raman absorbances due to the CN stretch are observed respectively at 2061.9 (2), 2061 (1); 2073.8 (2), 2074 (1); and 2083.3 (2), 2084 (1) cm^{-1}. The (near) degeneracy of the asymmetric and symmetric CN stretches, which has previously been noted[37] in linear bis(cyanato) complexes of Ag^+ and Hg^{2+}, is associated with a C–metal–C bond angle equal to (or close to) 180°. While in the bis(cyano) complexes of Ag^+ and Hg^{2+} ν_1 and ν_3 are within 6 and 1.5 cm^{-1}, respectively, in the equally linear $Au(CN)_2^-$ complex, the two bands are separated by 19 cm^{-1}. In the case of the ruthenium complexes of the present study, containing one molecule of solvent per metal atom, for which a cis configuration of the two NCS^- groups is clearly established, the symmetric and asymmetric CN stretches appear to be similarly nearly degenerate. This may arise as a consequence of the similarity in bonding properties of the four aromatic nitrogen atoms of the two bpy ligands and the two nitrogen atoms of the pseudoaromatic NCS^- groups, arranged in an octahedral array around the metal center. Further studies of this conjecture are currently under way. In this context, complexes of the type $ML_2(NCS)_2$, where M is a transition metal and L is a bidentate nitrogen-donor ligand, have been reported by Lever et al.,[38] who noted that the CN stretch of the pseudohalide ligand in the cis complexes appears as a single band in the IR spectrum at room temperature. It is only observed as a doublet (splitting ca. 6 cm^{-1}) at liquid-nitrogen temperature. In any event, the present crystallographic and infrared data clearly show that the observation of a single (fundamental) IR mode of the A–B vibration of compounds of the type A–B–M–B–A cannot be taken as unambiguously diagnostic of the presence of inversion symmetry in the molecular point group. The near degeneracy of the symmetric and asymmetric ν_{CN} stretches of the isothiocyanates of transition metals appears to be more general than has

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(30) March, F. C.; Ferguson, G. *Can. J. Chem.* **1971**, *49*, 3590.

(31) Konig, E.; Madeja, K.; Watson, K. J. *J. Am. Chem. Soc.* **1968**, *90*, 1146. Konig, E.; Watson, K. J. *Chem. Phys. Lett.* **1970**, *6*, 457.

(32) Fe: Sotofte, I.; Rasmussen, S. E. *Acta Chem. Scand.* **1967**, *21*, 2028 (correction: *Acta Chem. Scand.* **1968**, *22*, 1045). Co: Hartl, H.; Brudgam, I. *Acta Crystallogr.* **1980**, *B36*, 162. Ni: Porai-Koshitz, M. A.; Antsyshkina, A. N. *Sov. Phys.—Crystallogr.* (*Engl. Transl.*) **1960**, *3*, 694. Valach, F.; Sivy, P.; Koren, B. *Acta Crystallogr.* **1984**, *C40*, 957.

(33) Engelter, C.; Thornton, D. A. *J. Mol. Struct.* **1977**, *42*, 51. See also: Clark, R. J. H.; Williams, C. S. *Spectrochim. Acta* **1966**, *22*, 1081.

(34) Thompson, L. K. *Inorg. Chim. Acta* **1980**, *38*, 117.

(35) Caira, M. R.; Nassimbeni, L. R. *Acta Crystallogr.* **1975**, *B31*, 581.

(36) Engelter, C.; Hutton, A. T.; Thornton, D. A. *J. Mol. Struct.* **1978**, *44*, 23.

(37) Jones, L. H. *J. Chem. Phys.* **1957**, *26*, 1578; **1957**, *27*, 468, 665; *Spectrochim. Acta* **1963**, *19*, 1675.

(38) Lever, A. B. P.; Ramaswarry, B. S.; Simonson, S. H.; Thompson, L. K. *Can. J. Chem.* **1970**, *48*, 3076.

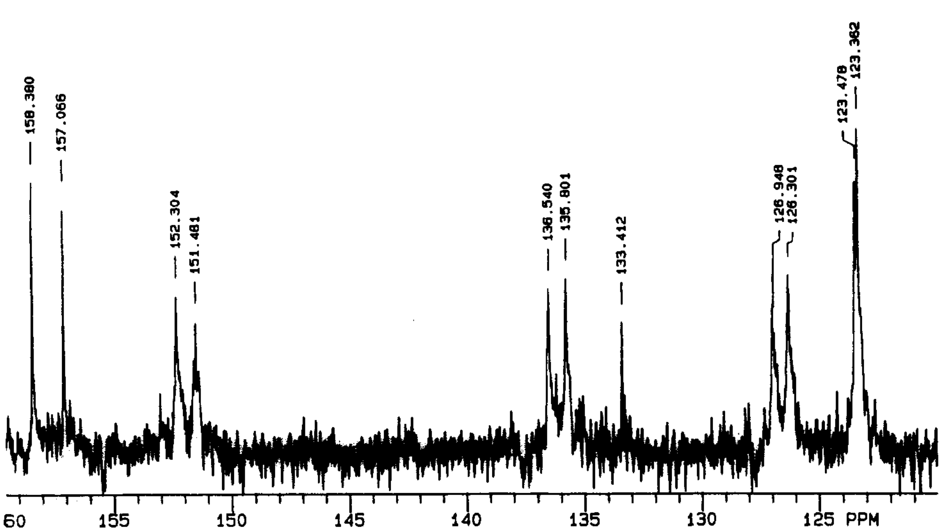

Figure 2. Portion of the ^{13}C NMR spectrum of $Ru(2,2'\text{-bpy})_2(NCS)_2$ in DMSO-d_6 at room temperature. The resonance at 133 ppm is assigned to the C atom of the pseudohalide ligand on the basis of systematic data for related ruthenium bipyridyl complexes.

Table V. ^{13}C NMR Results (ppm)

C atom	Ru $(2,2'\text{-bpy})_2(NCS)_2$/DMSO-$d_6$ 200 MHz	400 MHz	2,2'-bpy/ C_6H_6[a]	shift
6, 7	158.34	158.30	157.45	0.87
	157.03	156.98		−0.45
2, 11	152.27	152.24	150.1	2.2
	151.46	151.45		1.4
4, 9	136.50	136.47	137.3	−0.8
	135.74	135.74		−1.6
3, 10	126.94	126.91	124.4	2.5
	126.26	126.22		1.8
5, 8	123.44	123.40	121.8	1.6
	123.33	123.30		1.5
SCN^-	133.37	133.32		

[a] From ref 39.

previously been realized.

(c) NMR Spectroscopy. The unique role that the solvent plays in the structure of the title compounds is further implicated in the attempts to obtain suitable NMR spectra at room temperature. Although $Ru(2,2'\text{-bpy})_2(NCS)_2$ is sufficiently soluble in CH_3CN to afford distinctly colored solutions, no NMR spectra could be recorded for saturated (filtered) samples in this solvent. The solubility of $Ru(bpy)_2(NCS)_2$ in DMSO is approximately 17 times larger than it is in CH_3CN, as estimated from a comparison of the infrared spectra of (filtered) saturated solutions at room temperature, using the absorbance at 2100 cm^{-1} as a measure of solute concentration. This greater solubility in DMSO affords solutions that yield NMR spectra (both ^1H and ^{13}C) with an acceptable signal to noise ratio. A typical ^{13}C spectrum is shown in Figure 2. In this spectrum, there are 11 distinct carbon peaks, as expected for a cis octahedral structure in which the bpy ligand gives rise to 10 resolvable resonances, with the 11th being due to the NCS^- carbon atom. The 200-MHz data were acquired with both a 1- and a 10-s delay time, but no significant differences were noted between the two runs. The observed NMR data are summarized in Table V together with the corresponding values[38] for the bpy ligand in benzene, as well as the calculated shifts. No attempt was made in this study to further assign the ^{13}C chemical shifts with respect to the inequivalent C atoms in the ruthenium complex. The numbering scheme of the C atoms is the same as that in Figure 1. In this context it is interesting to note the long relaxation time (51 s)[39] for the 2,2'-C atoms of the pure ligand (in benzene), which makes it difficult to observe these resonances at normal scan frequencies. In the ruthenium complex, however, these resonances can be clearly resolved and are roughly of intensities equal to those of the other C atoms of the bpy ligand. The ^1H spectrum shows four doublet and 4 triplet resonances, in consonance to the spectra observed for $Ru(2,2'\text{-bpy})_2(Cl)_2$ by Birchall et al.,[40] on the basis of which they assigned a cis configuration to the dichloro complex in DMSO-d_6 at 30 °C. Clearly, the enhanced solubility of both the bis(chloro) and bis(isothiocyanato) complexes of the $(bpy)_2$ complexes of Ru(II) must be due to a nontrivial solute–solvent interaction in DMSO. The present structural data confirm unambiguously the incorporation of a solvate molecule in the solid isolated from solvents such as CH_3CN and DMSO, for which a dipolar interaction, especially with the pseudohalide ligand moiety, appears likely. In addition, these data confirm the cis configuration of the two pseudohalide ligands, both in solution in polar solvents and as solids containing one molecule of solvent per metal center. The (near) degeneracy of the infrared- and Raman-active CN stretching modes, which gives rise to the observed band profile discussed above, is a common feature of both the complex in the form of rigorously desolvated crystals and the complexes formed in the presence of a solvent that can be incorporated in the crystal structure, as shown in the present study.

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Supplementary Material Available: Tables SI, SII, SIV–SVIII, and SX, listing H atom parameters and anisotropic thermal parameters for **1**, positional parameters, H atom parameters, bond lengths, bond angles, and thermal parameters for **2**, and additional crystallographic data for **1** and **2**, and Figure SI, showing the numbering scheme and a stereoview for **2** (11 pages); Tables SIII and SIX, listing calculated and observed structure factors for **1** and **2** (26 pages). Ordering information is given on any current masthead page.

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(39) Breitmaier, E.; Bauer, G. In *Carbon-13 NMR Spectroscopy*, 3rd ed.; Breitmaier, E., Voelter, W., Eds.; VCH: Weinheim, West Germany, 1987; p 292.

(40) Birchall, J. D.; O'Donoghue, T. D.; Wood, J. R. *Inorg. Chim. Acta* **1979**, *37*, L461.