iron bond distance is as short as those of low-spin complexes.[30]

Deviations from ideal linear geometry of the Mn–C–N group, illustrated in Figure 6, are of interest in view of the nonideality in the Fe–C–N group in cyanohemoproteins.[31] The hemoprotein derivatives have apparent nonlinear Fe–C–N angles. Protein crystallographic studies show that the nitrogen atom is clearly displaced off the heme normal, but the poorly defined carbon atom position does not allow a clean distinction between a bent FeCN unit or a linear FeCN group tilted with respect to the N_4 plane. These nonideal geometries of the coordinated cyano ligand are presumed to result from constraints of the size and shape of the ligand-binding pocket. Similar deviations from ideality are seen in (carbon monoxy)hemoproteins.[32]

The Mn–C–N group in [Mn(TPP)(CN)] is distorted from ideal geometry by both bending and tilting. The Mn–C–N angle is 172.1 (5)°, but this bent group is further tilted off the normal to the porphyrin plane. The Mn–C_{25} vector is tilted by 5.75° from a vector perpendicular to the porphyrin plane. Thus the C_{25} atom is displaced 0.22 Å from the normal and N_5 is displaced by 0.47 Å. (This displacement would be 0.33 Å if the MnCN group was linear.)[33] However, the manganese atom is located directly above the center of the porphyrin hole. The distortion apparently results from packing interactions involving the nitrogen atom but not the carbon atom of cyanide. The most significant contact is between N_5 and the carbon atom of the chloroform solvate at 3.01 Å. The fact that both bending and tilting of the MnCN group are observed attests to the stiffness of the Mn–C bond. In [Mn(TPP)(CN)], where the Mn–C bond is unusually long and π bonding presumably somewhat weakened, the bending force constant apparently remains high. The bending force constant must be larger for a Fe–C_{CN} bond. This suggests that a bending distortion in the FeCN group will be difficult and that the distortion in the FeCN group of hemoproteins must predominantly result from a tilting mechanism as suggested by Deatherage et al.[31a]

Acknowledgment. We are pleased to acknowledge support of this research from the National Institutes of Health, Grant HL-15627.

Registry No. [Fe(TPP)(CN)(py)]·H_2O, 85135-21-3; [Mn(TPP)(CN)]·$CHCl_3$, 85135-22-4; Fe(TPP)(CN)(1-MeIm), 85135-23-5; K[Fe(TPP)$(CN)_2$], 73946-20-0; Mn(TPP)(OH), 85136-24-6.

Supplementary Material Available: Table III, anisotropic temperature factors for [Fe(TPP)(CN)(py)], Table V, anisotropic temperature factors for [Mn(TPP)(CN)], Table VIII, idealized hydrogen atom positions for [Fe(TPP)(CN)(py)], Table IX, idealized hydrogen atom positions for [Mn(TPP)(CN)], and listings of observed and calculated structure amplitudes (×10) for [Fe(TPP)(CN)(py)] and [Mn(TPP)(CN)] (57 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the Bis(pyridine) Adduct of a Dinuclear Rhodium(II) Complex with Trifluoroacetamidato Bridging Ligands

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Trifluoroacetamide reacts with $Rh_2(OOCCH_3)_4$ to produce the amidato-bridged complex $Rh_2(ONHCCF_3)_4$. The product is a mixture of four complexes that can be separated by liquid chromatography, with the distribution of complexes in the mixture being approximately 4% (band 1), 94% (band 2), 2% (band 3), and less than 1% (band 4). The complex in band 4 was not collected in this study because of the small amount present in the mixture. The molecular weights of the complexes in bands 1, 2, and 3 were determined by mass spectrometry and were all found to be the same, indicating they are three of the four possible geometric isomers. The visible spectra of all three isomers are similar, showing two bands shifted to higher energy relative to those of the corresponding dirhodium(II) carboxylate adducts. The ^{19}F NMR spectrum of the complex in band 1 shows three CF_3 resonances, suggesting this complex is the isomer with three N atoms and one O atom bonded to one rhodium and the reverse combination bonded to the other rhodium. The crystal structure of the bis(pyridine) adduct of the complex from band 2, $Rh_2(ONHCCF_3)_4(py)_2$, has been determined by X-ray crystallography. The compound crystallizes in the orthorhombic space group *Pnma* with four formula weights in the unit cell of dimensions $a = 15.523$ (4) Å, $b = 16.613$ (6) Å, and $c = 10.407$ (6) Å. The structure was solved by the Patterson method and refined to a final *R* value of 7.2%. This complex has two N and two O atoms on each rhodium cis to their own kind. A Rh–Rh bond distance 2.472 (3) Å was found, which is much longer than that in the corresponding carboxylato-bridged complex. The pyridine planes are coplanar, set 45° from the bridging ligand planes and bent slightly away from the NH groups. The average Rh–N_{py} distance of 2.29 Å is also significantly longer than that reported for the tetraacetato-bridged complex.

Introduction

The structure and chemical reactivity of dinuclear rhodium(II) complexes have been investigated extensively in recent years. Interest in these complexes stems from earlier controversy regarding the nature of the metal–metal interaction[1–4] and the interpretation of σ and π components of the rhodium–axial ligand bond.[5–11] The questionable nature of the

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Rh–Rh interaction arose from structural studies, which showed the Rh–Rh distance to be considerably shorter than that expected for a Rh–Rh single bond,[1] and spectroscopic measurements[12,13] coupled with theoretical calculations,[2,3,11] which indicated a bond order of 1. This problem has now been resolved in favor of the single bond, however, and the major concern of the more recent structural investigations has been the nature of the orbital interactions between the rhodium(II) dimer and the axial ligands and the effect this interaction has on the Rh–Rh bond.[6-8,10] There is no doubt that the axial ligands have a pronounced influence on the orbital pattern of the dimer system. A number of π-acidic ligands have been shown to produce considerable lengthening of the Rh–Rh distance, which is contrary to what would be predicted for π donation from the dimer system as described by Norman and Kolari.[2] Electron spin resonance studies by Kawamura and co-workers[14] on a number of cation radicals of bis(phosphine) adducts show the unpaired electron resides in an orbital of σ symmetry. Again, this finding is seemingly at odds with Norman's molecular orbital configurations for the diaquo adducts.[2] In an attempt to resolve this question, Bursten and Cotton[11] have reported results from Xα–SW molecular orbital calculations on the $Rh_2(O_2CH)_4(PH_3)_2$ complex, and they conclude that a strong σ donation by the phosphine ligands results in a higher occupied molecular orbital of Rh–Rh σ and Rh–P σ^* symmetry. This result is consistent with the ESR spectra of the cation radical of phosphine adducts. In addition, their result gave no indication of back-donation of π electron density to the phosphine ligands.

Bursten and Cotton's results clarify somewhat the picture regarding rhodium–axial ligand bonding and the effect this interaction has on the Rh–Rh bond for tetracarboxylato complexes. However, there are still many unanswered questions concerning this dimer system, particularly with regard to the role the bridging ligand plays in determining the electronic, structural, and chemical properties of the dirhodium(II) species. It is known that the preference of the rhodium(II) center toward different types of axial ligands can be profoundly altered by changes in the nature of the carboxylate bridges (O_2CR). For example, dimethyl sulfoxide coordinates through sulfur when R = methyl but through oxygen when R = CF_3.[15] Carboxylate anions can be replaced by other bridging anionic ligands to form new dinuclear rhodium(II) species such as $[Rh_2(CO_3)_4]^{4-}$,[16] $[Rh_2(SO_4)_4]^{4-}$,[16] and $[Rh_2(H_2PO_4)_4]$.[17] With the chelating anionic ligands acetylacetonate[18] and dimethylglyoximate[19] partial or complete exchange for carboxylate ions occurs to form dirhodium(II) complexes where the chelating ions are nonbridging. Few complexes have been synthesized with bridging ligands having donor atoms other than oxygen. Dikareva and co-workers[20] have reported the synthesis and structure of a thioacetato-bridged complex for which the Rh–Rh distance is much longer than for rhodium(II) acetate, but thioacetate complexes of rhodium(II) have proven difficult to study because of stability and solubility problems. Recently Cotton and Felthouse[21] published extensive structural information on seven dinuclear rhodium(II) complexes with 2-oxypyridine anions as bridging ligands, and two bonding combinations were observed for the bridging ion. One consisted of the dirhodium(II) unit complexed with four 2-oxy-6-methylpyridine bridging ligands such that Rh–N and Rh–O bonds were always trans to their own kind. The other consisted of three Rh–N bonds and one Rh–O bond on one rhodium and the reverse combination on the other. The Rh–Rh distance for these complexes is a little shorter than that observed for the acetate-bridged complex.

The synthesis of dinuclear transition-metal complexes with hetero donor atom bridging ions opens new avenues for the study of metal–metal-bonded systems. This is particularly true for the amidato ion. The amidato ion possesses the correct orbital symmetry to function as a bridging ion, offers the possibility for isomers where the two metal ions can be in the same or different electronic environments, and can be chemically altered at both the amide nitrogen and carbon atoms. Several years ago we attempted to prepare rhodium(II) complexes with acetamidato bridging ions, but we were not successful because of the instability of the dirhodium(II) systems under the extremely basic conditions necessary to extract the amide proton. However, we have recently reported the synthesis of a dirhodium(II) complex with four trifluoroacetamidato bridging ligands,[22] and in this paper we report the crystal structure and chemical properties of this complex.

Experimental Section

Chemicals. $Rh_2(OOCCH_3)_4$ was prepared from $RhCl_3{\cdot}3H_2O$ (Alfa Inorganics) by a known procedure.[5] Trifluoroacetamide was obtained from Aldrich Chemical Co. and purified by sublimation. All solvents used in this study were reagent grade quality.

Preparation of $Rh_2(ONHCCF_3)_4$. A 1-g quantity (2.26×10^{-3} mol) of $Rh_2(OOCCH_3)_4$ was mixed with 25 g (2.21×10^{-1} mol) of trifluoroacetamide in a 100-mL round-bottom flask. The flask was stoppered and placed in an oil bath at 140–150 °C. The mixture was magnetically stirred at this temperature for 5–6 h. The originally deep blue solution slowly turned reddish purple during the reaction. After the reaction was complete, the excess trifluoroacetamide was removed by sublimation, and the product was recrystallized from an acetone–water mixture. Elemental analysis of the product is in excellent agreement with the calculated values for $Rh_2(ONHCCF_3)_4$. Anal. Calcd: C, 14.68; N, 8.56; F, 34.84; Rh, 31.50. Found: C, 14.93; N, 8.52; F, 34.71; Rh, 31.70. The parent ion mass of the complex determined by LC–MS in the negative ion mode was 653, which corresponds to the dirhodium complex with one nitrogen proton ionized.

Separation of Rhodium(II) Complexes. The chromatographic system consisted of a Model 6000A solvent delivery system (Waters Associates), an RCM-100 radial compression module containing a 10-μm Radial-PAK CN column (Waters Associates), and a Model SP 8200 UV detector (Spectra-Physics) operated at 254 nm. The analog UV detector output was recorded on a Model 281 strip chart recorder (Soltex). Simultaneously, the signal from the detector was digitized at 1-s intervals by a Model ADC-12 QZ analog-to-digital converter (Analog Devices) interfaced to a Model 9830A digital computer (Hewlett-Packard). The mobile phase, isocratic methanol

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Table I. Summary of Data Collection and Processing Parameters

space group	*Pnma*, orthorhombic
cell const	$a = 15.523\ (4)$ Å
	$b = 16.613\ (6)$ Å
	$c = 10.407\ (6)$ Å
	$V = 2684$ Å^3
molecular formula	$Rh_2F_{12}O_4N_6C_{18}H_{14}$
mol wt	812.17
molecules/cell	$Z = 4$
density (calcd)	2.01 g cm^{-3}
abs coeff	$\mu = 12.6$ cm^{-1}
radiation (Mo Kα)	$\lambda = 0.71073$ Å
collection range	$4° \leqslant 2\theta \leqslant 50°$
scan width	$\Delta\theta = (1.00 + 0.35 \tan\theta)°$
max scan time	180 s
scan speed range	0.5–6.7° min^{-1}
total data collected	2708
independent data with $I > 3\sigma(I)$	1178
total variables	170
R $(\Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert)$	0.072
R_w $([\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w \lvert F_o\rvert^2]^{1/2})$	0.066
weights	$\sigma(F)^{-2}$

(HPLC grade, J. T. Baker Chemical Co.), was degassed by stirring under reduced pressure followed by a dry-nitrogen purge. A concentrated methanol solution of $Rh_2(ONHCCF_3)_4$ was injected (25 μL/injection), and the components were collected. The three collected fractions were concentrated and rechromatographed to achieve maximum purity.

Molecular Weight Determination of Rhodium(II) Complexes. An experimental LC-MS being developed by Dr. Marvin Vestal and co-workers[23-25] at this university was used to determine the mass of the rhodium(II) species present in bands 1, 2, and 3. A 15-μL sample of each band was introduced into the mass spectrometer by means of a high-pressure loop injector and chromatographic pump. The methanol solution of the complex entered the vaporizer through a stainless steel capillary tube that was electrically heated to 300 °C. The pumping rate of the effluent was 0.5 mL/min. Using a soft-ionization technique[24] and operating in the negative ion mode, we produced negatively charged parent ions. These ions were observed by a quadrupole mass filter and electron multiplier with a 2000-amu range. The analog output was passed through an A/D converter into a Finningan-INCOS 2300 data system.

Preparation of $Rh_2(ONHCCF_3)_4 \cdot 2py$. The complex isolated from band 2, $Rh_2(ONHCCF_3)_4$, was dissolved in methanol containing a slight stoichiometric excess of pyridine. Slow evaporation resulted in the formation of yellow crystals of the bis(pyridine) adduct of the complex.

X-ray Data Collection. Three attempts were made to collect single-crystal X-ray diffraction data, using three separate crystals of the bis(pyridine) adduct of the band 2 geometric isomer (vide infra). The first crystal decomposed very rapidly (<6 h), and the second, which was coated with a polymer spray, fared little better. The third crystal, however, showed no decomposition in the X-ray beam for several days, and this was enough time to collect a full set of data. The reason for this charmed behavior is not entirely clear at this time. All diffraction measurements were made with an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation monochromatized by a dense graphite crystal assumed to be ideally imperfect. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The Laue symmetry was determined to be *mmm*, and from the systematic absences noted, the space group was shown to be either *Pnma* or *Pn*2_1*a*. Intensities were measured by using the θ–2θ scan technique, with the scan rate depending directly on the net count obtained in rapid prescans of each reflection. Two standard reflections were monitored periodically during the course of the data collection as a check of crystal stability, and these varied by less than 4%. In reduction of the data, Lorentz and polarization factors were applied, but no absorption correction was made due to the low absorption coefficient and the fairly uniform dimensions of the crystal.

The structure was solved by interpretation of the Patterson map, which clearly indicated two unique rhodium atoms on the mirror plane of *Pnma*. This higher symmetry space group was initially chosen due to the symmetry of the molecule and because of the fact that most similar compounds reported have crystallized in centrosymmetric space groups. A subsequent statistical analysis of the normalized structure factors showed excellent agreement with theoretical values, and since the refinement converged to a reasonable R value, *Pnma* was assumed to be correct. The remaining non-hydrogen atoms were found in difference Fourier syntheses. There is only one half of the molecule in the asymmetric unit, the other half being generated by a mirror plane that contains the two rhodiums and bisects the N–Rh–N and O–Rh–O angles formed by attachment of the four trifluoroacetamidato ligands. The axial pyridine ligands lie perpendicular to this mirror. Before conversion to anisotropic temperature factors, it was decided to apply a simple test to make sure of the locations of the O and N atoms in the bridging ligands. With the R value at 10% the isotropic U's for O1, O2, N1, and N2 were 0.047, 0.045, 0.039, and 0.038 Å^2, respectively. When a new least-squares refinement was done with N scattering factors for O1 and O2, and O scattering factors for N1 and N2, the isotropic U's became 0.009, 0.005, 0.070, and 0.068 Å^2. This clearly indicated a lack of electron density at the O sites (refined as N) and an overabundance of density at the N sites (refined as O). The great disparity in value between these O and N temperature factors was enhanced by the fact that each atom has a mirror relative that was also carrying the wrong electron density. Thus, even if the true space group is *Pn*2_1*a*, the orientation of the ligands would certainly still be the same as in the *Pnma* case. The hydrogens could not be located and were entered at ideally calculated positions and held constant. Since the fluorine atoms displayed the usual high librational motion associated with terminal CF_3 groups, the least-squares program repeatedly attempted to position them too close to the central carbon atoms, and finally a bond distance constraint had to be applied to the C–F bonds to keep them all greater than 1.32 Å.

At this point in the refinement, with all expected atoms contributing, the R value was abnormally high, the pyridine temperature factors were slightly too large compared with those of other C and N atoms, and the difference map showed three unusually large spurious peaks in the vicinity of the pyridine nitrogens. The most logical conclusion was that the pyridine molecules were disordered over two positions, one perpendicular to the mirror plane of *Pnma* and the other coincident with the mirror. But no matter how the new positions were entered into the least squares (rigid body, etc.), half the atoms of the "new" pyridines would have very high thermal parameters, indicating no atom present. Also, when the population factors of the two groups were refined, the sum was greater than 100%, indicating the presence of more density than anticipated at some of the new positions. Finally, the temperature factors of all the atoms were held constant and each separate population factor was varied, and the following results were obtained: the original pyridine positions are occupied only 85% of the time; 15% of the time there are two other atoms present instead, both in the mirror plane, and one atom has about twice the electron density of the other. If we call these atoms A and B, where A is the donor atom bound to the rhodium ion, then from electron densities A can be C, N, O, or F and B is Si, P, S, Cl, or K. The best result is obtained when A–B corresponds to O–Cl; however, it is difficult to explain the source and existence of an unstable molecule such as HOCl. In fact it is difficult to explain any of the above combinations. Another possibility is that B could be a cation like K^+ and A could be OH^-. This is not too unreasonable since $Na[Rh_2(ONHCCF_3)X]$ (where X = F, Cl, Br) can be easily isolated. In any event, for our discussion we will call the molecule A–B. Entering one A–B fragment as OCl at either end of the molecule 15% of the time and pyridine 85% results in temperature factors that are comparable with those of the rest of the structure. With only 15% occupancy the atom A of each A–B behaves poorly and distance constraints had to be placed on the A atoms to keep them at chemically reasonable positions with respect to the Rh and B atoms (0.15 × ~8 electrons = ~1 electron, or about the same as a normal hydrogen). Although the exact nature of the A–B contaminant cannot be determined by purely crystallographic means due to its low occupancy, it is probably safe to say that it had a stabilizing effect on the crystal structure since this was the only crystal that lasted long enough in the X-ray beam for data to be collected. Since no other crystal we examined was found to have this impurity, there was no way to perform any of the normal chemical

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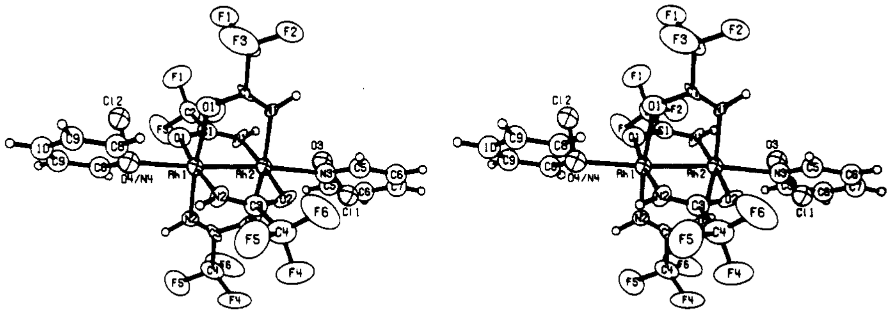

Figure 1. Stereoscopic view of the molecule showing the atom-labeling scheme. Hydrogens are numbered the same as the atom to which each is attached. The rhodiums and $HNOCCF_3^-$ ligands are shown as 40% equiprobability ellipsoids, with the others as spheres of arbitrary diameter. The two disordered ligands at both axial sites are shown simultaneously.

tests to ascertain its true identity.

After several cycles of full-matrix least squares, the refinement converged to the agreement factors listed in Table I. There were no unusually high correlations between any of the variables, with the exception of the distance constraints mentioned above. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree–Fock wave functions;[26] for hydrogen those of Stewart, Davidson, and Simpson were used.[27] The anomalous dispersion coefficients of Cromer and Liberman[28] were used for Rh and Cl (atom B). There seems to be little doubt that *Pnma* is the correct space group and the ligands are cis. Not only does the refinement converge to a resonable *R* value, the unitary structure factors show centric statistics, and the O and N atoms in the ligands refine to equivalent *U*'s but also there are several geometric symmetries that would not appear if the ligands were arranged trans. The bend of the independent CF_3 groups, the bend of the independent pyridines away from the amide nitrogens, the orientation of the two independent A–B groups, and the significantly shorter Rh–N bonds in comparison to the Rh–O ones will all be discussed below.

Results

High-Performance Liquid Chromatography–Mass Spectrometry. Even though the elemental analysis of the unseparated reaction product gave excellent agreement with the calculated values for $Rh_2(ONHCCF_3)_4$, the HPLC results showed the material to be a mixture of four complexes. The chromatogram presented in Figure 2 represents the analytical-scale separation of a 10-μL sample (2.8×10^{-7} mol) of $Rh_2(ONHCCF_3)_4$ with a CN bonded-phase column and isocratic methanol as the eluent. If it is assumed that all four complexes have nearly identical molar absorptivities at 254 nm, then the percentage of each complex in the mixture represented by bands 1, 2, 3, and 4 is approximately 4%, 94%, 2%, and less than 1%, respectively. In order to determine if the bands were the four possible geometric isomers of $Rh_2(ONHCCF_3)_4$ or simply complexes resulting from incomplete exchange of CF_3CONH^- for CH_3COO^-, each band was injected into a LC–MS and its molecular mass determined. The initial mass spectra obtained with the more abundant band 2 species dissolved in methanol displayed two negative molecular ions of mass 653 and 685. Mass 653 corresponds to $Rh_2(ONHCCF_3)_4$ that has lost one proton to yield $[Rh_2(ONHCCF_3)_3(ONCCF_3)]^-$, and mass 685 corresponds to the mono(methanol) adduct of the ionized complex. Later bands 1–3 were subjected to mass spectral analysis and the results are shown in Figure 3. A few days prior to the study the samples were dissolved in CD_3OD for ^{19}F NMR studies, and these solutions were used in the investigations. The mass spectra of the three samples showed that all three complexes have the same mass and that the N–H proton has been exchanged with deuterium. Again two major species were observed from the mass spectra: the negative parent ion and the mono(methanol) adduct. We are not sure why the two species observed for band 1 are one mass unit greater than those for bands 2 and 3. It could be due to the resolution of the mass spectrometer or the capture of an electron by the neutral complex without dissociation. In this paper we are reporting only the crystal structure of the bis(pyridine) adduct of the complex in band 2.

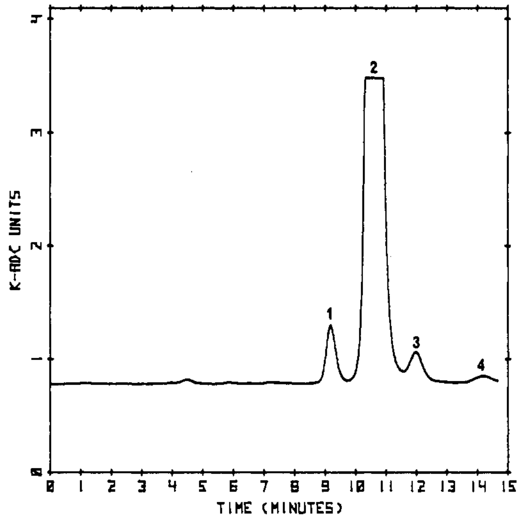

Figure 2. Chromatogram of the product resulting from the reaction of CF_3CONH_2 with $Rh_2(OOCCH_3)_4$. The amount of mixture injected to obtain a good chromatogram of the minor components resulted in band 2 being off scale.

Ultraviolet and Visible Spectra. The ultraviolet and visible spectra for bands 1–3 and the unseparated mixture of $Rh_2(ONHCCF_3)_4$ were obtained in a methanol solution. The visible spectra, shown in Figure 4, of each of the isomers shows two absorbances shifted approximately 40 nm in a hypsochromic direction relative to rhodium(II) acetate. The absorption maxima in the 350–400-nm region are not clearly defined in some cases due to overlap into the UV region. The UV spectra of the component in each of the separated fractions are essentially identical, showing a strong band at 232 nm ($\epsilon = 1.5 \times 10^4$) and a shoulder at 270 nm.

Nuclear Magnetic Resonance Studies. Sufficient quantities of the complexes in bands 1 and 2 were obtained for the ^{19}F NMR investigation. Chemical shifts were determined with use of an external $CFCl_3$–acetone-d_6 reference value of 0.00 ppm Our crystallographic study shows that each Rh in the complex constituting band 2 has two cis nitrogen and two cis oxygen donors. As expected, only one ^{19}F resonance at −74.3 ppm was observed for the complex. The complex in band 1 displayed three ^{19}F resonances at −74.2, −74.3, and −75.0 ppm with an area ratio of 2:1:1. The only geometric isomer that should have three non magnetically equivalent CF_3 groups with

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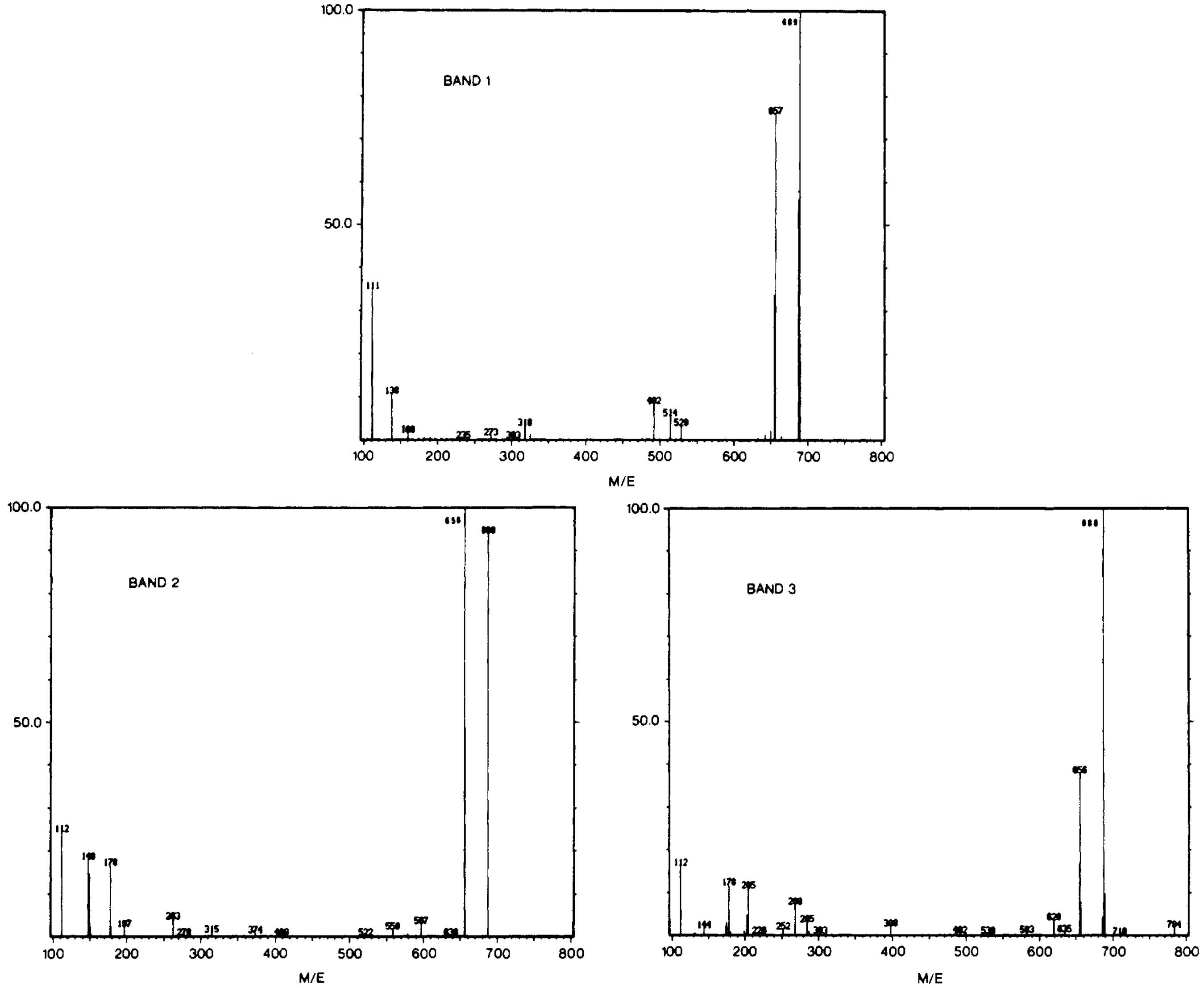

Figure 3. Mass spectra of the complexes in bands 1–3 from liquid chromatographic separation.

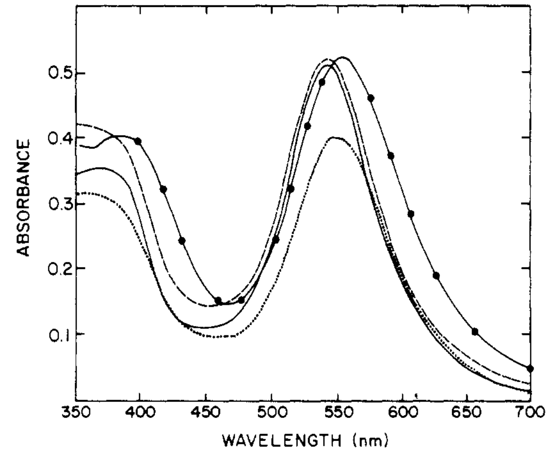

Figure 4. Visible spectra of complexes in band 1 (- - -), band 2 (—), and band 3 (···) and product mixture (—●—).

this area ratio is that with three nitrogens and one oxygen on one rhodium ion and the reverse combination on the other. The ^1H NMR spectrum of $Rh_2(ONHCCF_3)_4$ reveals a broad resonance at 6.71 ppm for the imide proton, which is shifted 2 ppm upfield from that of the free ligand.

X-ray Crystal Structure of the Bis(pyridine) Adduct of the Band 2 Complex. Bond lengths, angles, and torsion angles are listed in Tables II–IV, based on the final positional parameters.

Table II. Intramolecular Bond Distances (Å)

Determined Bonds			
Rh1-Rh2	2.472 (3)	N2-C3	1.16 (2)
Rh1-O1	2.12 (1)	C1-C2	1.55 (2)
Rh2-O2	2.12 (1)	C3-C4	1.56 (2)
Rh2-N1	2.01 (1)	N3-C5	1.32 (2)
Rh1-N2	1.98 (1)	C5-C6	1.40 (2)
Rh2-N3	2.31 (1)	C6-C7	1.31 (2)
Rh1-N4	2.26 (1)	N4-C8	1.31 (2)
O1-C1	1.28 (2)	C8-C9	1.40 (2)
O2-C3	1.31 (2)	C9-C10	1.35 (2)
N1-C1	1.19 (2)		

Constrained Bonds			
C-F	1.32-1.34	N-H	0.95
Rh-O3,O4	2.24-2.25	C-H	1.00
C1-O	1.45		

The atom-labeling scheme is shown in Figure 1, with hydrogens numbered the same as the atom to which each is attached. The band 2 complex is found to be the particular geometric isomer (of the four possible kinds) having the four trifluoroacetamidato ligands bridging the dirhodium(II) unit such that each rhodium binds to two oxygens and two nitrogens in a cis arrangement. With the Rh–Rh bond and the axial ligands included, the coordination about each Rh is essentially octahedral (see Table III). The Rh–Rh bond is a relatively long one, with a length of 2.472 Å. The two crystallographically unique bridging ligands show excellent agreement between

Table III. Intramolecular Bond Angles (deg)[a]

O1-Rh1-Rh2	87.1 (4)	N1-Rh2-N1′	87.7 (6)
N2-Rh1-Rh2	85.4 (5)	Rh1-O1-C1	115 (1)
O1-Rh1-N2	89.0 (6)	Rh1-N2-C3	126 (1)
O1-Rh1-O1′	90.1 (5)	Rh2-O2-C3	113 (1)
O1-Rh1-N2′	172.5 (6)	Rh2-N1-C1	123 (1)
O1-Rh1-N4	89.8 (5)	O1-C1-N1	129 (2)
O4-Rh1-Rh2	176 (1)	O2-C3-N2	128 (2)
N4-Rh1-Rh2	175.7 (4)	O1-C1-C2	105 (1)
N4-Rh1-N2	97.6 (6)	O2-C3-C4	103 (1)
N2-Rh1-N2′	90.9 (6)	N1-C1-C2	125 (2)
O2-Rh2-Rh1	87.6 (4)	N2-C3-C4	129 (2)
N1-Rh2-Rh1	86.3 (5)	Rh2-N3-C5	122 (2)
O2-Rh2-N1	91.4 (5)	N3-C5-C6	122 (2)
O2-Rh2-O2′	88.9 (5)	C5-C6-C7	122 (2)
O2-Rh2-N1′	173.8 (6)	Rh1-N4-C8	121 (2)
O2-Rh2-N3	88.1 (5)	N4-C8-C9	122 (2)
O3-Rh2-Rh1	176 (1)	C8-C9-C10	121 (2)
N3-Rh2-Rh1	173.8 (5)	Rh2-O3-C11	119 (3)
N3-Rh2-N1	98.1 (6)	Rh1-O4-C12	101 (3)

[a] The C-C-F angles average 112 (2)°, and the F-C-F angles average 107 (2)°.

Table IV. Selected Torsion Angles (deg)

O1-Rh1-Rh2-N1	−1.2	C8-N4-Rh1-N2	49.7
O1-Rh1-Rh2-O2′	179.3	C11-O3-Rh2-N1	136.1
O1-Rh1-Rh2-O2	90.4	C11-O3-Rh2-O2	44.7
O1-Rh1-Rh2-N1′	−89.1	C12-O4-Rh1-O1	45.1
N1-Rh2-Rh1-N2	−90.4	C12-O4-Rh1-N2	134.1
N1-Rh2-Rh1-N2′	178.3	N1-C1-C2-F2	−9.1
O2-Rh2-Rh1-N2	1.2	N2-C3-C4-F5	−6.2
N3-Rh2-Rh1-N4	180.0	O1-C1-C2-F1	−68.4
O3-Rh2-Rh1-O4	0.0	O1-C1-C2-F3	51.0
C5-N3-Rh2-N1	48.2	O2-C3-C4-F4	−66.6
C5-N3-Rh2-O2	−42.9	O2-C3-C4-F6	49.6
C8-N4-Rh1-O1	−39.3		

equivalent bonds and angles, with the averages being as follows: Rh–O, 2.12 Å; Rh–N, 2.00 Å; C–O, 1.30 Å; C–N, 1.18 Å; C–C, 1.56 Å; Rh–O–C, 114°; Rh–N–C, 125°; O–C–N, 129°; O–C–C, 104°; N–C–C, 127°; C–C–F, 112°; F–C–F, 107°. The sum of the angles about the trigonal carbons (C1 and C3) averages 360°, indicating planarity despite the severe distortions from ideality in the separate values. Due to crystallographic constraints, the axial pyridines are positioned so as to exactly bisect the O–Rh–N angles. As can be clearly seen in Figure 1, the principal axes of the pyridines are not collinear with the Rh–Rh bond but instead show Rh–Rh–N angles of 174 and 176°. The C6–C7 and C9–C10 bonds in the pyridines show the usual shortening due to lack of a correction for thermal libration; the remaining bond lengths are as expected. As mentioned in the Experimental Section, 15% of the time pyridine is replaced by A–B, which preferentially positions itself so as to bisect the O–Rh–O angles of the $Rh_2(ONHCCF_3)_4$ complex. There does not appear to be any intermolecular hydrogen bonding involving A–B, but there might be an intramolecular attractive force between the amide hydrogens and the nearby fluorines.

Discussion

It is well documented that the Rh–Rh and Rh–L_{ax} bond lengths are quite sensitive to the nature of the bridging ligands in dirhodium(II) complexes.[3-11,15,21,29] The majority of information available dealing with the interactions of the bridging ligand with the Rh_2^{4+} moiety results from studies involving the tetracarboxylato-bridged complexes. In this system the inductive effect of the bridging ligands can be studied by keeping the axial ligands constant and substituting different R groups on the carboxylate ion. It has been recognized for some time that synthesis and structural characterization of Rh_2^{4+} systems with a greater variety of bridging ligands are needed to fully clarify the questions of bridging constraint. In this regard the amidato bridging ligand is susceptible to a diversity of alteration by substitutions on the amide carbon and nitrogen atoms. To our knowledge, the compound reported here constitutes the first example of an amidato-bridged dirhodium(II) complex. Unfortunately, since this is the first structural study to be made on this particular bridging system, we are not in a position to make any truly meaningful comparisons at this time. In a broad context, however, several general observations can be made, especially with regard to the results of a recent study by Cotton and Felthouse involving the hetero donor atom bridging ligands 2-oxy-6-methylpyridine (mhp) and 2-oxy-6-chloropyridine (chp).[21]

In mhp and chp bridging systems, the Rh–O bonds are always shorter than the Rh–N bonds, whereas in our trifluoroacetamidato (tfaa) complex the opposite holds true (and with a much greater difference). This is not too surprising, considering mhp and chp contain a neutral pyridyl N while tfaa involves a negatively charged amide N. We also find in our system the Rh–Rh bond is about 0.09 Å longer than in the mhp and chp complexes. In fact, the value of 2.472 Å that we now report is among the longest yet seen in Rh_2^{4+} dimers having four bridging ligands. It is midway between the 2.55-Å value found in $Rh_2(OSCCH_3)_4(CH_3CSOH)_2$[30] and the 2.39 Å found in an earlier bridging system we reported.[31] It is clear that electron-withdrawing substituents on the bridging carboxylate ion, like CF_3, increase the Rh–Rh distance whereas electron-donating groups such as $(CH_3)_3C$ shorten the Rh–Rh bond.[29] However, this inductive effect is too small to account for the long Rh–Rh distance observed for the tfaa complex. It appears instead that the interaction between the strongly basic amide nitrogen and the Rh_2^{4+} dimer is responsible for the long Rh–Rh distance. One would expect that rhodium binding to the less electronegative N would result in an increase in electron density on the rhodium ion through σ donation and, if compared to the inductive effect produced by $(CH_3)_3C$ for carboxylato complexes, predict a decrease in the metal–metal distance. The unusually short Rh–N and C–N bonds suggest multiple bonding with the orbitally complex Rh_2^{4+} ion, and this could be the source of the Rh–Rh bond lengthening. Because of the complexity of the system and the myriad possibilities for hybridization and rehybridization upon interaction, detailed calculations on this complex are needed to further characterize the bonding in this system.

With such a long Rh–Rh bond, we would expect to find a shorter than usual Rh–L_{ax} bond; however, this is not the case. The average Rh–N_{py} length of 2.29 Å is significantly longer than that reported for the tetraacetato-bridged complex (2.23 Å),[6] which has a Rh–Rh distance of only 2.396 Å. Although this appears to contradict the usual trans effect observed in these complexes, since the present crystal structure shows a 15% disorder due to the unknown molecule A–B in the axial positions, we cannot have complete confidence in our Rh–L_{ax} distance at this time.

There are some unusual features in the geometry of the bridging ligands themselves that merit discussion. The most striking of these is the sharp bend of the CF_3 groups away from the amide nitrogens and toward the oxygens. This is probably related to another observation—that the orientation of the three fluorines is such that one is approximately in the NCO plane and on the same side as NH, while the other two are staggering the opposite oxygen. Since this is not at all the

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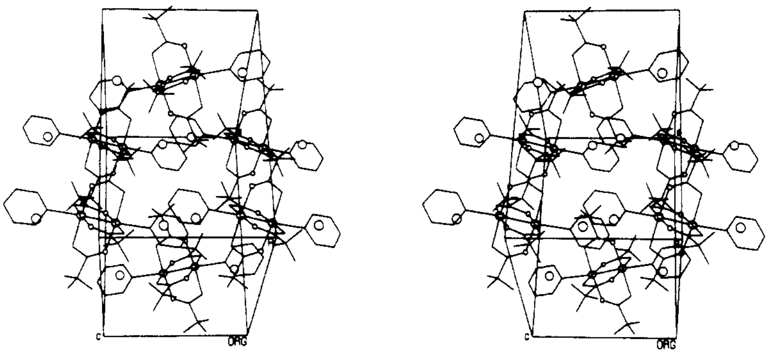

Figure 5. Stereoscopic view of the molecular packing in the unit cell with hydrogens omitted. Only the B sites of the A–B groups are shown, as large hollow spheres. The small hollow spheres in the ligands are the amide nitrogens. Note the close proximity of B sites, which precludes simultaneous occupancy.

position that would minimize van der Waals repulsions between nonbonded atoms, it must be assumed that there is some compensating force behind it, and the most plausible explanation would seem to be some manner of hydrogen bonding between NH and F. Under normal circumstances the F and H atoms would tend to mimimize the contact distance, but with geometric constraints preventing a favorable angle of approach in this case, the F backs off somewhat. The contact distances involved are F2···H1 = 2.33 Å and F5···H2 = 2.38 Å, both shorter than the sum of the van der Waals radii (2.7 Å) and indicative of an attractive force strong enough to overcome the normal tendency of the fluorines to adopt a staggered configuration with respect to the amide N.

Another indication that there might be some interaction between the amide hydrogen and the fluorines is the remarkably short C–N bond length. The average of 1.18 Å is unrealistic under the best of circumstances, being shorter than a pure double bond, and the usual explanation would be that the abnormal shortening is a mathematical artifact due to thermal libration of the nitrogen causing a distortion of the location of the atomic center by the least-squares routine. Such occurrences are common. In this case, however, the thermal motion is not unduly large, although there may be some strengthening of the C–N bond due to weakening of the N–H bond as caused by the H···F interactions. In any event, the CF_3 is certainly not behaving in the normal manner, such as found in the structure of $Rh_2(O_2CCF_3)_4(Me_2SO_2)_2$,[29] where the staggering with respect to that carboxylate is most efficient. The C–C–F and F–C–F angles in that complex average 111 and 108°, compared to our values of 112 and 107°, and so there is no unusual compression within the amide CF_3 units themselves. Other possible explanations for the unreasonably short C–N bonds might be the lack of an absorption correction applied to the data and/or the appearance of a false minimum in the least squares which both nitrogens fell into.

With regard to the axial ligands, it is interesting to note that the pyridine planes are coplanar, 45° from the bridging ligand planes. Such is not always the case in these types of complexes.[6] The Rh–Rh–N angles deviating from 180° is not at all unusual. Some Rh_2^{4+} complexes show very little bend,[10,15,21,29] while others show a substantial amount in those cases where some steric hindrance is involved.[10,21] In the present case, the pyridines always bend away from the NH groups, which is probably only coincidental since the amide hydrogens seem too far removed to have any effect on the axial ligands. As mentioned earlier, the A–B molecules take the place of pyridines 15% of the time on each side of the molecule but in slightly different locations with respect to the pyridines. It is important to point out, however, that, although it is quite possible to have both pyridines replaced on a single molecule, this would have highly segregative effects on the molecular packing. As shown in Figure 1, the B atoms always stagger themselves between the cis bridging oxygens of a given rhodium, and as can be seen in the packing diagram of Figure 5, the arrangement is such that adjacent molecules have the sites that might be occupied by B atoms pointing toward each other. Were two of these adjacent sites to be occupied simultaneously in the crystal, the B···B separation would be only 2.34 Å, which is chemically unreasonable. Unfortunately since the X-ray structure shows only the average atomic populations of a given site in the unit cell, we cannot ascertain what percentage of the molecules in this mixture had just one A–B and how many, if any, had two. The A–B molecules are probably the reason that this particular crystal was stable in the X-ray beam for a substantially longer amount of time than other batches of crystals that we examined (and that we assume were pure), but the mechanism behind this serendipity is not at all clear. At first it was assumed that some sort of NH···B hydrogen bonding was involved that added partial stability to the lattice, but it was soon found that the amide hydrogens are nowhere near the B atoms, and besides they are already much too busy with intramolecular bonding to fluorines. Unless B has some unusual affinity for pyridine π clouds (see Figure 5), we cannot explain the added stabilization caused by this 15% impurity.

In any event it is apparent that the major product of the reaction between $Rh_2(OOCCH_3)_4$ and CF_3CONH_2 is the isomer with two Rh–N and two Rh–O bonds on each rhodium ion cis to their own kind. The only isomer reported by Dikareva and co-workers[20] for the tetrathioacetato-bridged dimer also has the same cis arrangement of Rh–S and Rh–O bonds. This is not true however for the chp and mhp complexes reported by Cotton and Felthouse.[21] They report only the trans isomer for the complex where each rhodium(II) has two N and two O donors. These results raise some interesting questions with respect to the factors that determine the isomer distribution for these reaction systems. The distribution of isomers is probably related to both a thermodynamic preference and the mechanism of the exchange process. More detailed kinetics and thermodynamic studies are needed before we can answer these questions.

The visible spectra of the complexes separated by liquid chromatography and the unseparated mixture, shown in Figure 4, display only small shifts in the energy of the two transitions. Apparently, different arrangements of N and O bonded to the two rhodium(II) ions do not result in significant changes in the energy of the transitions. The carboxylato- and amidato-bridged dimers both show two bands in the visible region. The lower energy band is sensitive to the nature of the axial ligand, and shifts in this band are the source of the color changes. The higher energy band is relatively insensitive to axial perturbation. Norman and Kolari[2] have carried out calculations on the $Rh_2(OOCH)_4$ complex and assigned the lower energy band to a Rh–Rh $\pi^* \rightarrow$ Rh–Rh σ^* transition and the other band to a Rh–Rh $\pi^* \rightarrow$ Rh–O σ^* transition. The basic differences in the visible spectra of $Rh_2(ONHCCF_3)_4L_2$ and $Rh_2(OOCCH_3)_4L_2$ with a given axial ligand, L, are an ~40 and ~70 nm shift to higher energy of the lower and higher energy bands, respectively, for $Rh_2(ONHCCF_3)_4L_2$. Even though theoretical and experimental studies are needed, it is attractive to assign the lower energy band of $Rh_2(ONHCCF_3)_4$ to the $\pi^* \rightarrow \sigma^*$ transition and the band at ~380 nm to some type of $\pi^* \rightarrow$ Rh–O or Rh–N σ^* transition.

In conclusion, the molecular weight of the complexes (shown in Figure 2) in bands 1–3 are the same, and thus all three are probably geometric isomers. The complex in band 1 can be tentatively identified from the ^{19}F NMR spectrum as the isomer with three N atoms and one O atom on one rhodium and the reverse combination on the other. This complex shows three CF_3 resonances, which is consistent with such an isomer. The complex in band 2 is known from the structure determination reported in this paper. Band 3 is one of the remaining two possible isomers. We are presently working on several other amide systems, and preliminary results indicate that for a few systems relatively large amounts of all four isomers can be produced and isolated.

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Supplementary Material Available: Tables of observed and calculated structure factors and atomic coordinates and thermal parameters (8 pages). Ordering information is given on any current masthead page.

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Geometric Isomerism in Seven-Coordinate Tungsten(II) Mixed Carbonyl–Iodide–*tert*-Butyl Isocyanide Complexes[1,2]

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The crystal and molecular structures of two monoclinic forms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$ (**1** and **2**) and of $W(CO)I_2(t\text{-}C_4H_9NC)_4\cdot CHCl_3$ (**3**) have been determined. The coordination geometries of **1** and **2** are similar, approximating that of a 4:3 C_s piano stool. Two iodine atoms and a *tert*-butyl isocyanide carbon atom constitute the triangular cap, and the remaining four ligands constitute the tetragonal base. This isomer differs from that found in the previously studied orthorhombic form (**4**), in which one of the carbonyl ligands and the two iodine atoms form the triangular cap. Apart from their common 4:3 piano-stool structures, molecules in the three different crystalline forms of $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$ all have *cis*-WI_2 (W–I = 2.861 (2)–2.878 (1) Å; I–W–I = 85–88°) and *cis*-$W(CO)_2$ units (W–C = 1.87 (2)–2.00 (1) Å and C–W–C ~ 66–73°). The tungsten coordination geometry in **3** may be described as capped octahedral with the carbonyl group as the capping ligand (W–C = 1.93 (3) Å) and the two iodide atoms on the uncapped face (W–I = 2.876 (2) and 2.897 (2) Å; I–W–I = 87.9 (1)°). The W–CNR distances in the three structures range from 2.04 (3) to 2.19 (2) Å. Crystal data: for **1**, a = 9.362 (4) Å, b = 13.705 (2) Å, c = 19.797 (6) Å, β = 100.19 (3)°, space group $P2_1/n$, Z = 4, final R factor 0.037; for **2**, a = 9.773 (2) Å, b = 23.387 (6) Å, c = 11.918 (4) Å, β = 102.68 (2)°, space group $P2_1/n$, Z = 4, final R factor 0.065; for **3**, a = 9.763 (14) Å, b = 34.196 (10) Å, c = 11.484 (5) Å, β = 113.25 (6)°, space group $P2_1/n$, Z = 4, final R factor 0.050.

Introduction

Recently we have been studying the reductive coupling of coordinated alkyl isocyanide ligands in seven-coordinated d^4 molybdenum(II) and tungsten(II) complexes.[4] Although electronic effects are undoubtedly important in promoting this reaction,[2,4,5] the close nonbonded contacts between carbon atoms in a higher coordinate molecule having mostly linear ligands may also be a contributing factor. Since higher coordinated complexes of this kind are usually fluxional, it is difficult to probe their solution stereochemistries by conventional methods such as nuclear magnetic resonance spectroscopy. We have therefore undertaken an extensive and systematic X-ray crystallographic investigation of seven-coordinate group 6B metal isocyanide complexes in order to identify the solid-state structural patterns that might ultimately prove useful in designing reductive coupling reactions in solution.[6]

In the present paper we report the structures of two monoclinic crystalline forms (**1** and **2**) of $W(CO)_2I_2(tert\text{-}C_4H_9NC)_3$. An orthorhombic form (**4**) of this compound was previously shown to have the 4:3 tetragonal base–trigonal cap piano-stool geometry.[7] Preliminary work on a third monoclinic form (**5**) revealed a disordered structure that could not be refined. The low calculated density (1.565 g/cm^3 vs. 1.87–1.97 g/cm^3 for **1**, **2**, and **4**) of this crystal caused us to doubt whether it was characteristic of the bulk material in the sample, the analysis of which indicated it to be $W(CO)_2I_2(t\text{-}C_4H_9NC)_3$.[7] We have thus far been unable to obtain form **5** again, but attempts to do so have led reproducibly to **1**, **2**, and **4**. Forms **1** and **2** are shown here to be geometric isomers

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