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Gas-Phase Electron Diffraction Study of the Molecular Structure of (η-Cycloheptatrienyl)(η-cyclopentadienyl)niobium, Nb(η-C_7H_7)(η-C_5H_5)

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The molecular structure of [Nb(η-C_7H_7)(η-C_5H_5)] in the gas phase has been determined by electron diffraction at 470 K. The niobium atom is sandwiched by parallel, symmetric rings, with Nb–C distances (r_a) of 231.5(14) and 239.0(9) pm to the C_5H_5 and C_7H_7 rings, respectively. The C–H bonds of the C_5H_5 group are displaced 2.9(23)° out of the ring plane toward the niobium atom, while those of the C_7H_7 group are displaced 4.7(24)°, also toward niobium. The mean ring C–C bond length is 143.3(1) pm, with the bonds in the smaller ring being longer than those in the larger ring by 1.6(7) pm. These parameters are interpreted and related to those of the anion $[Nb(C_7H_7)(C_5H_5)]^-$ by consideration of the orbitals involved in bonding between the metal atom and the rings.

Introduction

Our understanding of the structure and bonding in η-cycloheptatrienyl complexes has advanced significantly with recent chemical, photoelectron spectroscopic, X-ray crystallographic, electrochemical, and theroetical studies.[1–5] We were interested in determining accurate gas-phase structural parameters for such compounds for use in calculations related to their electronic structure, *viz.*, the constitution of the metal–cycloheptatrienyl bond. Indeed, we now feel that, in its transition-metal complexes, this ligand is best thought of as donating a total of seven electrons to the complex while requiring three metal valence electrons to form a satisfactory M–(C_7H_7) bond.[3] This is in contrast to the widely assumed model of the coordinated $C_7H_7^+$ or "tropylium" ligand.

As part of this broader study, we describe here the molecular structure of [Nb(η-C_7H_7)(η-C_5H_5)] as determined by gas-phase electron diffraction: this is the first such structure of a cycloheptatrienyl compound to be reported. We have chosen this species since it sublimes very cleanly and because it allows us to compare the cycloheptatrienyl ligand with the cyclopentadienyl ligand in the same molecule.

Table 1. Weighting Functions, Correlation Parameters, and Scale Factors (Refinement 1)

camera height, mm	Δs, nm^{-1}	s_{min}, nm^{-1}	sw_1, nm^{-1}	sw_2, nm^{-1}	s_{max}, nm^{-1}	correlation param	scale factor (k)	electron wavelength, pm
198.6	4	40	60	192	224	0.0001	0.797(9)	5.732
258.1	2	20	40	142	166	0.4963	0.769(11)	5.671

Experimental Section

A crystalline sample of Nb(C_7H_7)(C_5H_5),[3] further purified by sublimation *in vacuo*, was heated in a high-temperature nozzle to provide sufficient vapor pressure for the experiment, which was carried out on the diffractometer at the University of Edinburgh.[6] With average sample and nozzle tip temperatures of 463 and 473 K, six plates were exposed, three each at middle (198.6 mm) and long (258.1 mm) camera distances. The electron wavelength, determined by analysis of the diffraction pattern of benzene, was 5.671 pm for the consistent second and third long-camera-distance plates which were used for the analysis, and 5.732 pm for the middle-camera-distance plates, all three of which were used. The long-camera-distance plates encompass an s range of 20–166 nm^{-1} and were traced in steps of 2 nm^{-1} on the Joyce-Loebl MDM6 microdensitometer at the SERC Daresbury Laboratory.[7] The middle-camera-distance plates have a range of 40–224 nm^{-1} and were traced at the same facility in steps of 4 nm^{-1}, yielding a total of 121 data points. Other experimental data are given in Table 1.

Results and Discussion

The reduction of the experimental data to molecular scattering curves and subsequent refinement of the molecular structure were carried out using the recently updated Edinburgh program system ED92. This is a

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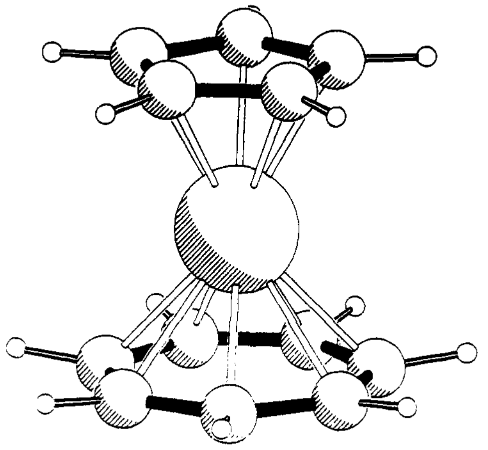

Figure 1. Perspective view of a molecule of $Nb(C_7H_7)(C_5H_5)$.

version of programs used previously,[8,9] modified to run under a UNIX operating system. The scattering factors used were those reported by Fink *et al.*[10] An *R* factor of less than 0.10 was obtained almost immediately using a standard coplanar sandwich model (see Figure 1) with distances estimated from previous crystallographic work on similar compounds[11] and mean amplitudes of vibration, *u*, estimated from previous electron diffraction studies of other sandwich compounds.[12-16] The final *R* factor of just over 0.05 (see Table 1) represents an excellent fit to the experimental data, borne out by the small difference intensity and radial distribution curves seen in Figures 2 and 3. The similarities among the pairs of C–C, Nb–C, and Nb···H distances for the five-membered and seven-membered rings, which vary much less than the combined mean amplitudes of vibration and are thus unresolved in the radial distribution curve (Figure 3), cause much correlation between parameters and complicate the analysis significantly. The model is set up to minimize these effects as much as possible by refining mean and difference values for both the C–C and the Nb–C distances in the two rings. In each case the parameter was a weighted mean, taking into account the greater multiplicities of distances for the seven-membered ring. The C–H distance (assumed to be the same for both rings) is the fifth parameter, with separate out-of-plane displacement angles for the hydrogen atoms in both rings making up the sixth and seventh parameters. Negative displacement angles represent distortions of the C–H bonds toward the niobium atom. An eighth parameter, defined as the angle between the local C_5 and C_7 axes perpendicular to the carbocyclic rings, was added at one stage, to check that the rings were parallel.

The parameters obtained in two separate refinements are presented in Table 2, with selected distances and their *u* values in Table 3. Table 4 is the correlation matrix for the procedure in which the greater number of parameters was refined.

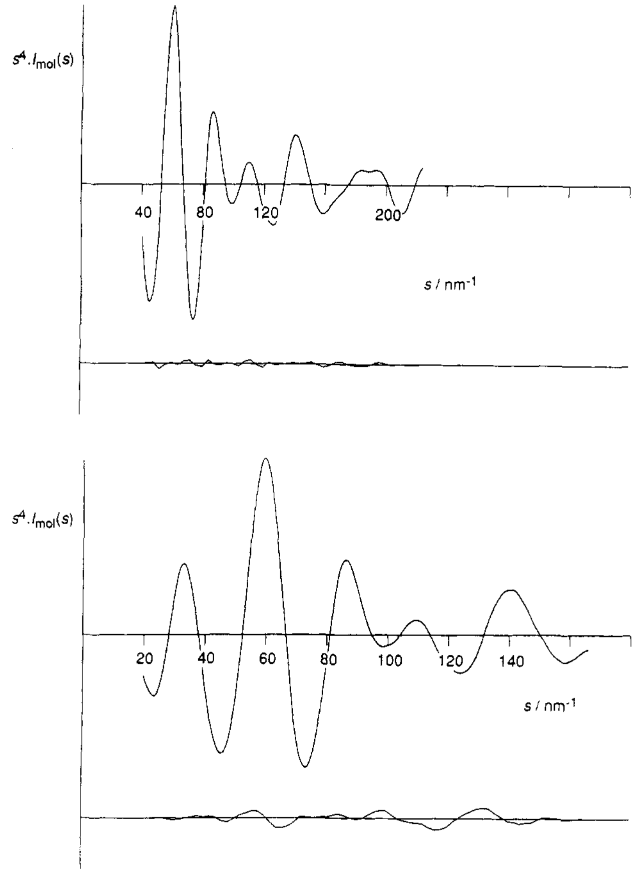

Figure 2. Observed and final weighted difference molecular scattering intensity curves for $Nb(C_7H_7)(C_5H_5)$, recorded at camera distances of (a, top) 199 and (b, bottom) 258 nm. The difference curve corresponds to refinement 1.

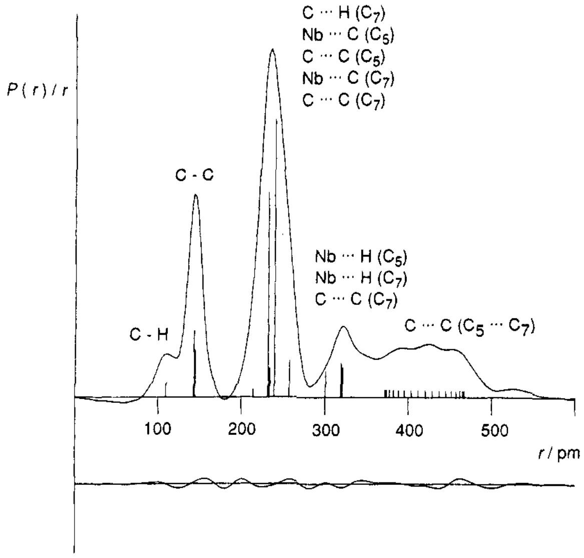

Figure 3. Observed and final weighted difference radial distribution curves, $P(r)/r$. Before Fourier inversion the data were multiplied by $s\ \exp(-0.00002s^2)(Z_{Nb} - f_{Nb})(Z_C - f_C)$. The difference curve corresponds to refinement 1.

First we consider the barrier to internal rotation of the C_5H_5 and C_7H_7 rings relative to each other. Here the fact that the rings are different actually simplifies the picture, since the resulting 35-fold barrier to rotation means that

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Table 2. Geometrical Parameters for $Nb(C_7H_7)(C_5H_5)$[a]

	refinement 1[b]	refinement 2[c]
p_1: r(C–C)(mean)/pm	143.3(1)	143.3(1)
p_2: Δr(C–C)[d]/pm	–1.6(7)	–0.9(4)
p_3: r(Nb–C)(mean)/pm	235.8(2)	235.8(2)
p_4: Δr(Nb–C)[d]/pm	7.4(24)	11.1(5)
p_5: r(C–H)	109.2(6)	109.4(6)
p_6: C–H tilt (C_5H_5)/deg	–2.9(23)	–1.2(20)
p_7: C–H tilt (C_7H_7)/deg	–4.7(24)	–6.9(19)

[a] Values in parentheses are estimated standard deviations, obtained in the least-squares analyses. [b] Procedure in which u(Nb–C) was refined. [c] Refinement in which u(Nb–C) was fixed at 8.0 pm. [d] Value for seven-membered ring minus that for five-membered ring.

Table 3. Interatomic Distances (r_a/pm) and Amplitudes of Vibration (u/pm)[a]

		refinement 1		refinement 2	
		r	u	r	u
		C_5H_5 Ring			
r_1	Nb–C	231.5(14)	9.2(15)	229.3(4)	8.0 (fixed)
r_2	Nb···H	300.2(27)	13.0 (fixed)	300.8(28)	13.0 (fixed)
r_3	C–C	144.3(4)	4.0 (3)	143.9(3)	4.0(3)
r_4	C···C	233.4(7)	5.5 (fixed)	232.8(5)	5.5 (fixed)
		C_7H_7 Ring			
r_5	Nb–C	239.0(9)	9.2 (tied to u_1)	240.5(2)	8.0 (fixed)
r_6	Nb···H	318.7(20)	13.0 (fixed)	317.7(24)	13.0 (fixed)
r_7	C–C	142.7(3)	4.0 (tied to u_3)	142.9(2)	4.0 (tied to u_3)
r_8	C···C	257.1(5)	5.5 (fixed)	257.6(3)	5.5 (fixed)
r_9	C···C	320.6(6)	6.0 (fixed)	321.2(4)	6.0 (fixed)
		Both Rings			
r_{10}	C–H	109.2(6)	8.8(7)	109.4(6)	8.9(8)
		Inter-ring			
	C···C	372–468	18.0 (fixed)	372–468	18.0 (fixed)
	C···H	371–537	20.0 (fixed)	371–537	20.0 (fixed)
	H···H	358–616	20.0 (fixed)	358–616	20.0 (fixed)

[a] Values in parentheses are estimated standard deviations, obtained in the least-squares analyses.

Table 4. Least-Squares Correlation Matrix ×100 for Refinement 1[a,b]

p_4	p_7	u_1	k_1	
69	–70	–79		p_2
	–64	–94		p_4
		–52		p_6
		63		p_7
			60	u_3

[a] Only elements with absolute values >50 are included. [b] For refinement 2, the only element >50% was p_2/p_3 = 77%.

the barriers themselves must be extremely small. Indeed, separate models were tried with the rings first eclipsed (defined to be the conformation in which a C–H bond in one ring eclipsed one C–H bond in the other ring) and then staggered, and absolutely no difference was observed in the quality of the fit, confirming this idea. The staggered model was used subsequently.

The radial distribution curve shown in Figure 3 has four main peaks which are resolved below the long, broad region corresponding primarily to the inter-ring C···C and C···H distances. The largest contains the two Nb–C distances; the parameter representing the difference between these distances is very strongly correlated to their mean amplitudes of vibration (see Table 4), here constrained to be equal to one another. Because of this correlation, the variation of the R factor as a function of the difference between the Nb–C distances was studied to ensure that there was no other minimum, for the opposite sign of this difference with comparable u values. In varying this difference from −15 to +15 pm, the u values do indeed track very closely, rising as the difference approaches 0 and then symmetrically falling away again. There is only one minimum, however, with the Nb–C distance to the seven-membered ring longer than that to the five-membered ring by 7.4(24) pm as shown in Table 2.

The resulting Nb–C u value is 9.2(1.5) pm, which is slightly larger than any metal–carbon u value mentioned in the electron diffraction studies cited above (primarily 3d metals), except for $Mn(C_5H_5)_2$, which has a very large electron imbalance of 5, according to the concept of Gard *et al.*[14] On the basis of their mass spectra, Van Oven *et al.*[17] anticipate a stronger metal to carbon bond for 4d or 5d (e.g. Zr, Nb) than for the corresponding 3d metal compounds, which would also be more consistent with a smaller rather than a larger u value. However, the experimental result is within 1 standard deviation of our estimated starting value of 8.0 pm. The second set of results in Table 2 shows the results of fixing the Nb–C amplitude of vibration at this estimated value. Uncertainties in the individual Nb–C distances plummet, by a factor of about 5, which makes things look much more definitive. The point is that we do not know this u value, nor at present do we have a good way of predicting it reliably; therefore, the former large uncertainties are a more honest appraisal of our knowledge, at least on the basis of this experiment.

It is interesting, therefore, to compare the current results with single-crystal X-ray diffraction measurements on the related sandwich anion[2] in [K(18-crown-6)][$Nb(C_7H_7)(C_5H_5)$]. As can be seen from Figure 1, in the neutral species the perpendicular distance from the niobium atom to the plane of the C_7H_7 ring is significantly less than that to the C_5H_5 plane, by 22.9 ppm (173.4 *vs* 196.3 pm): this is a consequence of the larger size of the C_7 ring. This is also true for the somewhat distorted anion, although the difference between these distances is much larger, 48 pm (167 *vs* 215 pm). In the anion the distance between the niobium atom and the carbon atoms of the C_5H_5 ring (243 pm) is longer than the average Nb–C distance to the C_7H_7 ring, which is only 231 pm, whereas in the neutral species investigated here, the Nb–C distance to the C_7H_7 ring is longer by 7 pm. For the anion, however, the coordination of the potassium ion to the cycloheptatrienyl ring could affect the bond lengths significantly, complicating such a direct comparison. These observations may be rationalized by considering the extra electron in the anion, which occupies the primarily nonbonding niobium d_{z^2} orbital. The extra charge on the metal atom increases back-donation to the rings and decreases donation from the rings. As the main bonding interaction between the metal and the C_7 ring is back-donation of δ symmetry, the bonding is strengthened in the anion, whereas the major interaction between the metal and the C_5 ring is π donation, which is therefore weakened in the anion, in accord with the observed pattern of Nb–C distances.

The second largest peak in the radial distribution curve (Figure 3) contains the bonded C–C distances, which are in principle different in the five- and seven-membered rings. Even though the difference here is smaller than that between the Nb–C distances, the uncertainty is also smaller, in both refinements. The cross-ring distances, which are of course different in the pentagon and heptagon, help to define this difference parameter, even though they

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occur in peaks dominated by either Nb–C or Nb···H scattering. Thus, the cyclopentadienyl C–C distance was determined to be slightly longer than the cycloheptatrienyl distance, but the difference is significant, even at the 2σ error level. The effect on the *R* factor of changing this difference parameter from −2.5 to +2.5 pm in steps of 0.5 pm was then investigated, and this confirmed that the negative value to which the parameter converged was indeed the only minimum. A typical C–C distance in a coordinated cyclopentadienyl ring from electron diffraction studies is 143 pm,[12–14] compared to an average crystallographic C–C distance in cycloheptatrienyl rings of *ca.* 140 pm.[3] Allowing for an expansion in the latter of 1–2 pm when measured by electron diffraction in the gas phase,[13,14] the bond length in the seven-membered ring should still be slightly shorter than in a five-membered ring, as observed in the present study. A recent crystallographic compilation[11] gives an *average* C–C distance in η^5-C_5H_5 rings as 139.7 pm and an *average* C–C distance in η^7-C_7H_7 rings as 140.8 pm. There is, of course, a range of values for both distances, and the gas-phase results given here are consistent with these ranges.

The value for *u*(C–C) was obtained by assuming a common value for all C–C bonds. Attempts to refine amplitudes of vibration for the nonbonded C···C intra-ring distances were not successful. They were therefore fixed at values based on results obtained in earlier electron diffraction studies of related compounds.[12–16]

The next largest well-defined peaks in the radial distribution curve are those due mainly to Nb···H scattering and the distinctive C–H peak just above 100 pm. The C–H peak is the least complicated and yielded both a bond length and an amplitude of vibration which are reasonable within the stated uncertainties. The Nb···H peak is sizable due to the large scattering power of Nb, but the two component distances are both functions of the Nb–C and C–C distances and the C–H displacement angles and are consequently correlated with one another. Persistent but unsuccessful attempts were made to refine Nb···H *u* values (again constrained to be equal), so these were also out of necessity left fixed at estimated values. The C–H displacement angles are more well-behaved, however, converging in all cases, even if with understandably large esd's. The parametric dependence of *r*(Nb···H) on the Nb–C distances means that the displacement angles are sensitive to the value used for *u*(Nb–C), as seen in Table 2, but other amplitudes of vibration had relatively small effects on these angles. In both refinements, however, the hydrogen atoms are displaced toward the niobium atom, with a larger displacement found for the cycloheptatrienyl hydrogen atoms. This is to be expected, since for shorter Nb–ring plate distances the metal-directed p_z orbitals would bend further toward the metal in order to improve overlap with the appropriate metal d orbitals, thus causing the C–H groups also to bend further inward.[18] The displacement angle in crystalline Ti(η-C_7H_7)(dmpe)Et is −8.6°, whereas a variety of displacement angles in cyclopentadienyl complexes discussed by Gard *et al.*[14] range only from −3.7 to +1.5° (using the sign convention defined earlier).

In our recent photoelectron spectroscopic study of the electronic structure of [Nb(η-C_7H_7)(η-C_5H_5)] we have assumed that the planes of the rings are parallel.[3] A parameter relating to bending at the niobium atom was put into the model to test this hypothesis. Once again it was not possible to refine this parameter, but a series of refinements in which this angle was fixed at values from 0 to 10° in steps of 2° and from 0 to 30° in steps of 5° showed the *R* factor to be a minimum in both cases at 0° (i.e. parallel). This result is consistent with the crystal structure of the 18-electron anion, in which the angle between the planes is very small, and certainly no more than could be caused by intermolecular forces in the crystal.

Finally, all 18 inter-ring C···C *u* values (see Table 3) were combined and refined as a single parameter. The corresponding distances are quite evenly distributed. Although this refinement was unstable, it was found that the lowest *R* factor was obtained with an amplitude of vibration of 18 pm.

Conclusions

The first molecular structure of a gaseous cycloheptatrienyl complex is reported. The niobium atom in (η-cycloheptatrienyl)(η-cyclopentadienyl)niobium is bonded symmetrically to parallel C_5H_5 and C_7H_7 rings, in a classical sandwich structure. The distance between niobium and the carbon atoms in the seven-membered ring is longer than that between niobium and the cyclopentadienyl carbon atoms, the reverse of the situation in the analogous anion. The C–H bonds in both rings are bent toward the metal atom. All the observed structural parameters are consistent with the established molecular orbital picture of the bonding in compounds of this type.

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