Preparation and Structure of Tetraphenylarsonium Tricyclooctatetraeneniobium, $[As(C_6H_5)_4][Nb(C_8H_8)_3]$

L. J. Guggenberger* and R. R. Schrock*

Contribution No. 2224 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898.

Received January 10, 1975

Abstract: Three moles of $[K^+]_2[C_8H_8]^{2-}$ react with $NbCl_5$ to give $K^+[Nb(C_8H_8)_3]^-$. Salts containing $[Li(THF)_4]^+$ and $[As(C_6H_5)_4]^+$ can be prepared by metathesis while $[Li(THF)_4]^+[Ta(C_8H_8)_3]^-$ is best prepared from $[Li(THF)_4]^+[Ta(C_6H_5)_6]^-$ and C_8H_8 in refluxing THF. Crystals of $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$ are monoclinic, the space group is $P2_1/c$, cell dimensions are $a = 12.996$ (16) Å, $b = 22.377$ (26) Å, $c = 14.371$ (23) Å, and β equals 115.51 (11)°. Observed and calculated densities for four formula units per cell are 1.40 and 1.39 g cm^{-3}, respectively. Phenyl rings were constrained as rigid bodies in the final refinements; the final conventional R equaled 0.077 for 2663 observed reflections. Three cyclooctatetraene (COT) ligands are coordinated to Nb and each has approximate $C_s(m)$ point symmetry. One COT is described as η^4-bonded, but is partway along the "reaction coordinate" interconverting η^4- and η^3-bonded COT ligands; the other two are the only examples of η^3-bonded COT ligands in a mononuclear species. We discuss COT conformations in several transition metal complexes in some detail.

Cyclooctatetraene complexes are known for nearly every transition metal[1a] as well as for several lanthanides[1b] and actinides.[1c] It is one of the most versatile carbocyclic ligands and can coordinate as a monoene (η^2, two-electron donor), diene (η^4, four-electron donor), triene (η^6, six-electron donor), or as a "tetraene" (η^8, eight-electron donor or ten-electron donor if viewed as a dianion). Its conformations vary from the strain-free, unconjugated "tub", to intermediate folded conformations where two or three coordinated double bonds form a separate ligand plane (with or without conjugation), to the completely planar, conjugated "dianion". Small energy differences between them may account in part for cyclooctatetraene's "fluxional" behavior on the NMR time scale in most mononuclear complexes.[2]

We are evaluating the possibility of generating new group 5 organometallic chemistry via cyclooctatetraene complexes. None has been prepared previously. We report here the preparation of one new class of complexes, $[M(C_8H_8)_3]^-$ (M = Nb,Ta), and a crystal structure of one of its members, $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$.

Experimental Section

Synthesis. Air and moisture must be strictly excluded during all operations. $[K^+]_2[C_8H_8]^{2-}$ solutions were prepared by stirring 39 g of potassium metal pieces and 52 g of C_8H_8 in ca. 1 l. of tetrahydrofuran overnight.

1. Preparation of $K^+[Nb(C_8H_8)_3]^-$. $NbCl_5$ (20 g) in 100 ml of toluene was cooled to −78°C. $[K^+]_2[C_8H_8]^{2-}$ (485 ml, 0.46 *M* in THF) was added over a period of 0.5 hr with stirring and the flask subsequently warmed to room temperature. Potassium chloride was removed by centrifugation in gas-tight polypropylene bottles and extracted twice with ca. 600 ml of THF, centrifuging each time. The three solutions were combined and filtered, and the volume was decreased to ca. 200 ml in vacuo. After standing for an hour at 0°, filtration gave fine purple-black crystals; yield 23 g (70%). The product may be recrystallized by halving the volume of a saturated THF solution in vacuo followed by standing at −30° overnight.

Anal. Calcd for $C_{24}H_{24}NbK$: C, 64.86; H, 5.44; Nb, 20.90; K, 8.80. Found: C, 64.17; H, 5.47; Nb, 21.07; K, 8.15. ^1H NMR (τ, CD_3CN) 5.13 (s).

Recrystallization of a 1-g sample from ca. 20 ml of hot diglyme gave 0.7 g of small, almost black crystals of $[K\{CH_3OCH_2CH_2)_2O\}]^+[Nb(C_8H_8)_3]^-$.

Anal. Calcd for $C_{30}H_{38}O_3NbK$: C, 62.27; H, 6.62; K, 6.76. Found: C, 61.66; H, 6.53; K, 7.11.

2. Preparation of $[Li(THF)_4]^+[Nb(C_8H_8)_3]^-$. Finely ground LiCl (1.3 g) was dissolved in 400 ml of THF and 13.1 g of $K^+[Nb(C_8H_8)_3]^-$ was added. After stirring 1 hr the KCl was filtered off and the volume decreased to ca. 200 ml in vacuo. Filtration gave shiny purple-black plates (13 g). Further volume reduction and filtration gave 1.6 g of additional product; total yield 14.6 g (85%). Recrystallization from acetonitrile gives $[Li(CH_3CN)_x]^+[Nb(C_8H_8)_3]^-$ (x unknown); the reverse gives $[Li(THF)_4]^+[Nb(C_8H_8)_3]^-$.

Anal. Calcd for $C_{40}H_{56}O_4NbLi$: C, 68.56; H, 8.06; Nb, 13.26; Li, 0.99. Found: C, 67.84; H, 8.06; Nb, 13.34; Li, 0.93; K <0.18. ^1H NMR (τ, CD_3CN) 5.20 (24, s, C_8H_8), 6.35 (16, m, THF), 8.22 (16, m, THF); uv-visible (in THF) ϵ_{553} 5000, ϵ_{315} 26000.

3. Preparation of $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$. $K^+[Nb(C_8H_8)_3]^-$ (5.0 g) and $[As(C_6H_5)_4]^+Cl^-$ (4.0 g) were stirred in 100 ml of dichloromethane for 10 min. The solution was filtered, the solvent removed in vacuo, and the residue washed with ethanol and diethyl ether; yield 7.3 g (82%). The product can be recrystallized from dichloromethane.

Anal. Calcd for $C_{48}H_{44}NbAs$: C, 73.10; H, 5.62. Found: C, 72.50; H, 5.57. ^1H NMR (τ, CD_2Cl_2) 1.9–2.5 (20, m, phenyl), 5.13 (24, s, C_8H_8). The spectrum is unchanged at −95°.

4. Preparation of $[Li(THF)_4]^+[Ta(C_8H_8)_3]^-$. A THF solution of $[Li(THF)_4]^+[Ta(C_6H_5)_6]^-$ (2.0 g) and cyclooctatetraene (3.0 g) was refluxed in the dark under nitrogen for 1 day. The solution was filtered and the volume decreased to ca. 10 ml in vacuo. Standing 1 hr at −30° followed by filtration gave 200 mg of purple-black plates. Addition of diethyl ether (10 ml) to the filtrate and standing 3 days at −30°C yielded 180 mg of additional product; total yield 0.38 g (23%).

Anal. Calcd for $C_{40}H_{56}O_4TaLi$: C, 60.91; H, 7.16; Ta, 22.94; Li, 0.88. Found: C, 60.92; H, 7.08; Ta, 25.17; Li, 1.01. ^1H NMR (τ, THF-d_8) 5.10 (24 relative to THF, s).

5. Preparation of $[As(C_6H_5)_4]^+[Ta(C_8H_8)_3]^-$. $[Li(THF)_4]^+[Ta(C_8H_8)_3]^-$ (90 mg) was dissolved in 10 ml of ethanol and 60 mg of $[As(C_6H_5)_4]^+Cl^-$ in 10 ml of ethanol was added immediately. Fine crystals were filtered off, dissolved in ca. 5 ml of dichloromethane, and recrystallized as small, thin, intense wine-red plates by addition of diethyl ether; yield 80 mg (80%).

The ^1H NMR spectrum of $[As(C_6H_5)_4]^+[Ta(C_8H_8)_3]^-$ in CD_2Cl_2 is essentially identical with that of the corresponding niobium species.

6. The Reaction of $[M(C_8H_8)_3]^-$ with CO. Treatment of $K^+[Nb(C_8H_8)_3]^-$ (1.0 g) in THF with CO (50 atm, 110°, 2 hr) gave a yellow solution. Removing all volatiles left $K^+[Nb(CO)_6]^-$ (0.54 g) as golden needles. The condensate contained 2.8 mol (per Nb) of C_8H_8 (by GLC). The diglyme adduct, $\{K[(CH_3OCH_2CH_2)_2O]_3\}^+[Nb(CO)_6]^-$ (ref 3), was isolated by recrystallization from diglyme. Similar results were observed for salts containing other cations. $[Ta(C_8H_8)_3]^-$ reacted similarly to give $[Ta(CO)_6]^-$ (ref 3).

Cell and Intensity Data. Crystals of $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$ are monoclinic with cell dimensions a = 12.996

(16), Å, b = 22.377 (26) Å, c = 14.371 (23) Å, and β = 115.51 (11)°. These parameters were obtained by least-squares refinement of eight reflections carefully centered on the diffractometer. The systematic extinctions, $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, establish the $P2_1/c$ space group. Observed and calculated densities for four molecules per cell are 1.40 and 1.39 g cm^{-3}, respectively. There is no space group imposed molecular symmetry.

A prismatic crystal approximately 0.20 × 0.25 × 0.41 mm was enclosed in a capillary and used for data collection. It was mounted on a Picker four-circle automatic diffractometer with the −202 axis, which is close to the long axis of the crystal, along the diffractometer ϕ axis. Zirconium-filtered Mo radiation (λ 0.7107 Å) was used to measure 3683 reflections (2θ max = 40°) including the symmetry-equivalent $hk0$ and $\bar{h}k0$ sets which were averaged. The θ(crystal)-2θ(counter) technique was used with a scan rate of 1°/min and a 2θ scan length of 2.25° plus the wavelength dispersion. Backgrounds of 15 sec were measured before and after each peak.

Standard reflections indicated the crystal deteriorated slightly with time and the data were corrected accordingly; the maximum correction was 2% in F_o. The data were not corrected for absorption effects. The linear absorption coefficient for Mo Kα radiation is 12.7 cm^{-1}; θ-2θ scans as a function of ϕ at ψ = 90° showed a maximum change in F_o of 2.5%. Structure factor errors were estimated as previously described.[4] Structure factors with $F_o < 2\sigma(F_o)$ were given zero weight in the refinements.

Structure Solution and Refinement. The structure was solved by "heavy-atom" techniques starting with the Nb and As atom positions which were located on a Patterson map. The cation's phenyl rings were treated as rigid groups to reduce the number of variables in the refinement. Rigid-body distances were fixed at 1.397 Å for C–C and 1.0 Å for C–H. The R value $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ was 0.069 for the 1407 strongest reflections. The model consisted of all nonhydrogen atoms with isotropic temperature factors and four rigid phenyl groups each with a single group temperature factor.

An electron density difference map showed evidence for many hydrogen atoms. All were included, but not refined, in calculated positions (C–H = 1.0 Å) with fixed isotropic temperature factors (6.0 Å^2). The group refinements continued with variable isotropic temperature factors for each carbon atom. The final refinements were done in two sections: (a) the scale factor and all parameters for the Nb, As, C(11)–C(18), and four rigid phenyl groups; (b) the scale factor and all parameters for the Nb, As, C(21)–C(28), and C(31)–C(38) atoms. Final R values for the 2663 "observed" reflections are 0.077 for R and 0.069 for R_w, $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. The corresponding values for all the data (3490 reflections) are 0.127 for R and 0.073 for R_w. A final electron density difference map showed peaks only for $|\rho| \leq 0.6$ e$^-$; the largest remaining peaks were in the vicinity of the phenyl rings.

Atomic scattering factors for neutral atoms were used.[5] The Nb and As atom form factors were corrected for the real and imaginary parts of the anomalous scattering.[6] The $\Sigma w(|F_o| - |F_c|)^2$ function was minimized in the refinement.[7]

Final positional and thermal parameters are given in Table I. Individual group atom parameters are given in Table II and all hydrogen atom positions are listed in Table III. A list of observed and calculated structure factors (×5) is available.[8]

Results and Discussion

Preparation and Properties. The dianion of cyclooctatetraene has been used successfully to prepare COT complexes of primarily the early transition metals (e.g., Ti(η^8-C_8H_8)(η^4-C_8H_8), ref 9), metals in the actinide series (e.g., U(η^8-C_8H_8)$_2$, ref 1c), and metals in the iron triad (e.g., Ru(bicyclo[2.2.1]hepta-2,5-diene)(η^6-C_8H_8), ref 10). This technique is cleaner and more predictable than that employing reducing agents such as aluminum alkyls in the presence of COT and seemed particularly suitable for preparation of Nb and Ta COT complexes.

Addition of 3 mol of $[K^+]_2[C_8H_8]^{2-}$ in tetrahydrofuran to a suspension of $NbCl_5$ in toluene at −78° followed by warming to room temperature gives an intense purple-black color characteristic of $[Nb(C_8H_8)_3]^-$ (ϵ_{553} 5000, ϵ_{315} 26000). The potassium salt, $K^+[Nb(C_8H_8)_3]^-$, can be isolated from this solution in high yield and $[Li(THF)_4]^+$ or $[As(C_6H_5)_4]^+$ salts by subsequent metathesis with LiCl or $[As(C_6H_5)_4]Cl$, respectively. $[Li(THF)_4]^+[Nb(C_8H_8)_3]^-$ is nearly pyrophoric, decomposes rapidly in dichloromethane, and reacts violently with methanol and water. $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$ reacts less readily with air in the solid state and only slowly with methanol in dichloromethane. The reactivity of $K^+[Nb(C_8H_8]^-$ is intermediate.[11]

$[Li(THF)_4]^+[Ta(C_8H_8)_3]^-$ is best prepared from $[Li(THF)_4]^+[Ta(C_6H_5)_6]^-$ (ref 12) and cyclooctatetraene in refluxing THF. The reaction may be viewed as a stepwise decomposition with replacement of lost phenyl groups by cyclooctatetraene ligands, though in detail it is complex. The major organic product is biphenyl with smaller yields of $C_8H_7(C_6H_5)$, $C_8H_9(C_6H_5)$, terphenyl, and possibly triphenylene, according to mass spectral analysis. Direct preparation from $[Li^+]_2[C_8H_8]^{2-}$ and $TaCl_5$ requires a tedious and low yield separation from LiCl. Pure $K^+[Ta(C_8H_8)_3]^-$ has not yet been isolated even though the presence of $[Ta(C_8H_8)_3]^-$ is confirmed by ^{1}H NMR and by its reaction with CO (vide infra). Impure $K^+[Ta(C_8H_8)_3]^-$ and LiCl in THF gives pure $[Li(THF)_4]^+[Ta(C_8H_8)_3]^-$ in low yield only after many recrystallizations. The properties of $[Li(THF)_4]^+[Ta(C_8H_8)_3]^-$ are similar to those of the Nb analog.

The ^{1}H NMR spectra of $[M(C_8H_8)_3]^-$ salts show only one sharp singlet at ca. τ 5.1 due to C_8H_8. In one instance, $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$ in CD_2Cl_2, cooling to −95° produced no significant spectral changes. A single signal for a given C_8H_8 ligand is commonly observed whenever it is bound to a single metal. Therefore, either all the ligands are identical, e.g., $[Nb(\eta^4\text{-}C_8H_8)_3]^-$, or structurally nonequivalent C_8H_8 rings also readily interconvert.

Reactions. We briefly investigated reactions of $[M(C_8H_8)_3]^-$ salts with typical donor ligands, hydrogen, carbon monoxide, and electrophiles. They react sluggishly with tertiary phosphines, phosphites, and 1,2-bis(dimethylphosphino)ethane (dmpe) in refluxing tetrahydrofuran to give brown, uncharacterized powders and with neither H_2 (1 atm) nor CO (1 atm) to any appreciable extent in several hours under similar conditions. At ca. 100° and 100 atm, however, reaction with hydrogen gives ca. 3 mol of cyclooctane and a black, insoluble, pyrophoric material. At 100° and 50 atm, carbon monoxide gives ca. 3 mol of cyclooctatetraene and $[M(CO)_6]^-$ salts. Not surprisingly, acids and $[C(C_6H_5)_3]^+$ react instantly at room temperature. In the presence of dmpe approximately 1 mol of cyclooctatetraene is produced and species of the type $M(C_8H_8)(C_8H_8E)$(dmpe)(E = electrophile) can be isolated. A description of this class of compounds will be presented in a future publication.[13]

Crystal Structure. Crystals of $[As(C_6H_5)_4]^+[Nb(C_8H_8)_3]^-$ were best suited for an X-ray structural investigation.

The Anion. The anion's structure is shown in Figure 1; the thermal ellipsoids are plotted at the 30% probability level. Magnitudes of the principal axes are given in Table I. Interatomic distances and angles are shown schematically in Figure 2 while some remaining nonbonding contacts and bond lengths and angles in the cation are given in Table IV.

The three COT ligands are arranged trigonally about niobium. Two are η^3-bonded, COT 1 by C(11), C(12), and C(18) and COT 2 by C(21), C(22), and C(28). One shorter (2.230 (3) Å av) and two longer (2.436 (7) Å av) Nb–C distances are present in each case. The third is η^4-bonded by C(31), C(32), C(33), and C(38) with two shorter (2.261 (12), 2.342 (14) Å) and two longer (2.468 (15), 2.683 (17)

Table I. Final Positional and Thermal Parameters (×10⁴) for $[As(C_6H_5)_4][Nb(C_8H_8)_3]$ [a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$\langle u\rangle$[b]
Nb	−0.08644 (9)	0.20334 (5)	0.06667 (9)	42.8 (9)	13.6 (3)	50.3 (9)	−0.6 (5)	17.4 (7)	2.5 (4)	(0.171, 0.182, 0.216)
As	0.38011 (11)	0.42976 (6)	0.15753 (10)	55.4 (11)	14.1 (3)	44.3 (10)	−2.2 (5)	20.3 (9)	1.9 (5)	(0.179, 0.194, 0.208)
C(11)	−0.2750 (10)	0.1917 (6)	−0.0055 (13)	32 (11)	16 (4)	85 (14)	−7 (5)	−3 (10)	−1 (7)	(0.129, 0.210, 0.315)
C(12)	−0.2506 (11)	0.1685 (6)	−0.0856 (11)	84 (14)	17 (4)	58 (12)	−12 (6)	−7 (11)	5 (6)	(0.176, 0.195, 0.335)
C(13)	−0.2272 (12)	0.1114 (7)	−0.1117 (11)	96 (15)	23 (5)	61 (12)	−9 (7)	13 (11)	−3 (6)	(0.205, 0.246, 0.303)
C(14)	−0.2217 (12)	0.0555 (7)	−0.0730 (12)	108 (16)	24 (5)	54 (13)	−4 (7)	−4 (12)	−7 (6)	(0.181, 0.254, 0.339)
C(15)	−0.2196 (12)	0.0306 (6)	0.0144 (15)	103 (16)	14 (4)	93 (16)	−9 (6)	13 (14)	3 (7)	(0.181, 0.246, 0.344)
C(16)	−0.2159 (11)	0.0559 (7)	0.1057 (13)	79 (14)	23 (5)	92 (15)	−12 (7)	17 (12)	15 (7)	(0.187, 0.232, 0.343)
C(17)	−0.2196 (11)	0.1146 (8)	0.1391 (11)	57 (13)	29 (5)	86 (14)	−1 (7)	20 (11)	11 (7)	(0.200, 0.244, 0.311)
C(18)	−0.2486 (11)	0.1707 (7)	0.0942 (13)	54 (13)	28 (5)	89 (15)	−18 (6)	31 (11)	0 (7)	(0.146, 0.274, 0.297)
C(21)	−0.0129 (10)	0.2949 (5)	0.0803 (12)	57 (12)	12 (3)	90 (14)	−4 (5)	22 (12)	6 (6)	(0.158, 0.203, 0.296)
C(22)	−0.0731 (12)	0.2911 (6)	−0.0288 (12)	88 (15)	14 (4)	92 (14)	7 (6)	45 (12)	16 (6)	(0.161, 0.237, 0.298)
C(23)	−0.1853 (16)	0.3090 (6)	−0.1004 (11)	150 (20)	15 (4)	71 (13)	−1 (7)	40 (15)	15 (6)	(0.151, 0.272, 0.334)
C(24)	−0.2785 (14)	0.3350 (6)	−0.0949 (13)	82 (17)	13 (4)	78 (15)	−3 (6)	−13 (12)	8 (6)	(0.172, 0.194, 0.358)
C(25)	−0.3097 (12)	0.3451 (6)	−0.0140 (16)	73 (14)	15 (4)	105 (17)	3 (6)	29 (15)	3 (7)	(0.195, 0.227, 0.313)
C(26)	−0.2625 (13)	0.3321 (6)	0.0867 (15)	85 (17)	17 (4)	99 (15)	−11 (6)	54 (14)	−4 (6)	(0.180, 0.237, 0.294)
C(27)	−0.1586 (14)	0.3093 (6)	0.1578 (12)	85 (16)	28 (5)	83 (13)	−8 (7)	32 (13)	2 (6)	(0.229, 0.262, 0.289)
C(28)	−0.0518 (11)	0.2988 (6)	0.1586 (10)	71 (14)	17 (4)	67 (12)	1 (6)	17 (11)	0 (5)	(0.209, 0.215, 0.268)
C(31)	0.0235 (11)	0.1224 (6)	0.0810 (18)	52 (13)	5 (3)	155 (21)	11 (5)	21 (15)	−3 (7)	(0.069, 0.206, 0.394)
C(32)	0.0391 (12)	0.1344 (8)	0.1829 (17)	53 (14)	27 (5)	121 (19)	12 (7)	23 (14)	28 (8)	(0.168, 0.236, 0.372)
C(33)	0.0911 (13)	0.1808 (7)	0.2482 (14)	79 (16)	22 (4)	137 (18)	16 (7)	67 (14)	30 (7)	(0.179, 0.200, 0.374)
C(34)	0.1833 (12)	0.2185 (6)	0.2628 (10)	68 (14)	23 (4)	67 (12)	13 (6)	25 (11)	4 (6)	(0.189, 0.245, 0.268)
C(35)	0.2428 (11)	0.2334 (6)	0.2093 (15)	48 (13)	18 (4)	106 (16)	−3 (5)	23 (13)	−5 (6)	(0.181, 0.215, 0.317)
C(36)	0.2258 (11)	0.2252 (7)	0.1073 (14)	39 (13)	31 (5)	94 (15)	−1 (6)	32 (12)	0 (7)	(0.153, 0.280, 0.287)
C(37)	0.1427 (14)	0.1977 (7)	0.0274 (12)	95 (16)	32 (5)	69 (13)	24 (8)	52 (13)	6 (7)	(0.170, 0.238, 0.327)
C(38)	0.0516 (12)	0.1571 (8)	0.0128 (13)	53 (14)	30 (5)	103 (16)	5 (7)	23 (12)	−22 (8)	(0.183, 0.222, 0.357)

Group	Atoms[c]	x_c	y_c	z_c	ϕ	θ	ζ
1	CR(11)–CR(16)	0.3511 (4)	0.4045 (2)	0.3702 (4)	1.812 (6)	−0.575 (4)	1.487 (6)
2	CR(21)–CR(26)	0.4638 (4)	0.3025 (2)	0.0992 (4)	3.188 (18)	1.325 (4)	5.123 (18)
3	CR(31)–CR(36)	0.5774 (5)	0.5323 (2)	0.2039 (4)	4.016 (5)	−0.451 (5)	0.223 (5)
4	CR(41)–CR(46)	0.1346 (4)	0.4699 (2)	−0.0295 (4)	2.818 (4)	−0.079 (4)	3.958 (4)

[a] The estimated standard deviations here and in other tables are given in parentheses. The anisotropic thermal factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Root-mean-square amplitudes of vibration (Å) along the principal axes of the anisotropic ellipsoid. [c] x_c, y_c, z_c are the group centers in fractional coordinates and ϕ, θ, ζ are orientation angles for the groups in radians. The group description is described by C. Scheringer, *Acta Crystallogr.*, 16, 546 (1963), and is similar to that used by R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

Table II. Carbon Atom Positions and Refined Thermal Parameters for the Rigid Groups

Atom	x	y	z	B(Å^2)
CR(11)	0.3627	0.4177	0.2802	3.0 (3)
CR(12)	0.4569	0.4220	0.3760	4.4 (3)
CR(13)	0.4454	0.4088	0.4660	5.5 (3)
CR(14)	0.3396	0.3914	0.4603	5.4 (3)
CR(15)	0.2454	0.3871	0.3645	5.6 (4)
CR(16)	0.2569	0.4003	0.2745	3.8 (3)
CR(21)	0.4279	0.3567	0.1232	3.0 (3)
CR(22)	0.4017	0.3427	0.0207	4.2 (3)
CR(23)	0.4376	0.2885	−0.0033	4.6 (3)
CR(24)	0.4998	0.2482	0.0752	4.3 (3)
CR(25)	0.5259	0.2622	0.1777	4.7 (3)
CR(26)	0.4900	0.3165	0.2017	3.9 (3)
CR(31)	0.4919	0.4895	0.1825	3.6 (3)
CR(32)	0.4897	0.5421	0.2338	3.8 (3)
CR(33)	0.5752	0.5850	0.2553	4.8 (3)
CR(34)	0.6628	0.5752	0.2254	5.2 (3)
CR(35)	0.6650	0.5225	0.1740	5.3 (3)
CR(36)	0.5796	0.4797	0.1525	4.2 (3)
CR(41)	0.2396	0.4530	0.0488	2.9 (3)
CR(42)	0.2201	0.5126	0.0170	3.7 (3)
CR(43)	0.1150	0.5296	−0.0613	4.5 (3)
CR(44)	0.0295	0.4870	−0.1078	4.7 (3)
CR(45)	0.0490	0.4274	−0.0760	4.0 (3)
CR(46)	0.1541	0.4104	0.0023	3.9 (3)

Å) Nb-C distances; the differences within the sets are due to the unusual Nb-COT 3 geometry which appears to be nearly midway along the "reaction coordinate" to an η^3 geometry for COT 3.

The bond distances should be compared with those from Nb to other C_π systems. The shortest are 2.10 (2) Å in (η^5-C_5H_5)(PH_3)Nb[HCPh(CPh)$_3$C(=NH)CH_3][14] and 2.297 (3) Å in [(η^5-C_5H_5)(C_5H_4)NbH]$_2$;[15] the former contains an unusual allylic fragment and the latter a bridging C_5H_4 ligand. The Nb-C distance to ethylene in ($\eta^5C_5H_5$)$_2$Nb(C_2H_5)(C_2H_4)[16] is 2.299 (21) Å. Observed Nb-C distances to η^5-C_5H_5 rings are 2.398 (4) Å in [(η^5-C_5H_5)(C_5H_4)NbH]$_2$,[15] 2.402 (5) Å in (η^5-C_5H_5)$_2$Nb(C_2H_5)(C_2H_4),[16] 2.44 Å in (η^5-C_5H_5)Nb(CO)[(C_6H_5)$_4C_4$][(C_6H_5)$_2C_2$],[17] 2.45 Å in {(η^5-C_5H_5)Nb(CO)[(C_6H_5)$_2C_2$]}$_2$,[18] and 2.46 Å in (η^5-C_5H_5)Nb(CO)[(C_6H_5)$_2C_2$]$_2$.[19] The shorter bond lengths to the central carbons on COT 1 and COT 2 are therefore on the low end of the observed range while the 2.683 (17) Å distance to COT 3 is longer than generally observed.

The coordination geometry is shown in more detail in Figure 3. The anion has nearly $C_s(m)$ point symmetry; the view in Figure 3a is normal to the idealized mirror plane. The trigonal disposition about niobium is defined by the dihedral angles between normals to coordination planes which pass through bound carbons of each ligand (118.0–120.9° Table V). The shape of COT 3 is well-defined by two planes, one passing through C(33) to C(38) and the second (the coordination plane) through C(31), C(32), C(33), and C(38). The dihedral angle between their normals is 26.4°. COT 1 and COT 2 are "dish-shaped" with angles between the four planes (e.g., C(11), C(12), C(18); C(12), C(13), C(17), C(18); C(13), C(14), C(16), C(17); C(14), C(15), C(16)) as follows for both COT's (plane normals given in Table V). The sum of dihedral angles for each is approximately equal to the dihedral angle in COT 3.

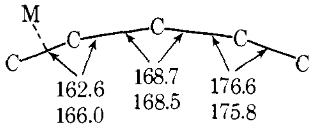


Figure 3b is a view with the normal to the idealized mirror plane vertical; this is a front view of Figure 3a rotated slightly about the vertical axis to reduce overlap. The largest deviation from $C_s(m)$ point symmetry is caused by a twisting of COT 3. The mirror plane ideally would pass through C(21), C(25), Nb,C(11), C(15), and the midpoints of C(31)-C(32) and C(35)-C(36), or alternatively, through C(31) and C(35) if an η^3 description of COT 3 were chosen.

An important point to remember here is that [Nb(C_8H_8)$_3$]$^-$ is a fluxional molecule. Only one sharp ^{1}H NMR singlet is observed since in solution the bound COT's scramble. The energy of the pathway by which they interconvert is probably quite low. Therefore packing forces could stabilize ligand conformations in the solid state which are probably close to, but not necessarily precisely on, the energy surface minimum for ligand conformations in solution. In this context one could argue that COT 3 is partway along the η^4 to η^3 "reaction coordinate" which probably typifies the type of dynamic processes operating in solution.

Cation Structure. The cation's structure is shown in Figure 4. Pertinent distances and angles are listed in Table IV. It is a regular tetrahedron with As-C distances equal to 1.89 Å and average C-As-C and As-C-C angles equal to

Table III. Hydrogen Atom Positions for [As(C_6H_5)$_4$] [Nb(C_8H_8)$_3$]

Atom[a]	x	y	z	Atom	x	y	z
H(11)	−0.3205	0.2301	−0.0238	H(37)	0.1399	0.2109	−0.0450
H(12)	−0.2508	0.2012	−0.1327	H(38)	−0.0068	0.1537	−0.0664
H(13)	−0.2063	0.1121	−0.1744	HR(12)	0.5326	0.4345	0.3800
H(14)	−0.2193	0.0205	−0.1192	HR(13)	0.5129	0.4118	0.5346
H(15)	−0.2226	−0.0161	0.0191	HR(14)	0.3314	0.3819	0.5248
H(16)	−0.2148	0.0258	0.1589	HR(15)	0.1696	0.3746	0.3604
H(17)	−0.1943	0.1188	0.2162	HR(16)	0.1894	0.3972	0.2059
H(18)	−0.2527	0.2056	0.1419	HR(22)	0.3572	0.3716	−0.0354
H(21)	0.0758	0.2974	0.1105	HR(23)	0.4189	0.2784	−0.0767
H(22)	−0.0249	0.2705	−0.0594	HR(24)	0.5255	0.2093	0.0580
H(23)	−0.2064	0.3032	−0.1796	HR(25)	0.5704	0.2333	0.2338
H(24)	−0.3367	0.3484	−0.1631	HR(26)	0.5087	0.3265	0.2751
H(25)	−0.3863	0.3681	−0.0418	HR(32)	0.4270	0.5491	0.2553
H(26)	−0.3179	0.3448	0.1188	HR(33)	0.5736	0.6226	0.2921
H(27)	−0.1627	0.2883	0.2205	HR(34)	0.7240	0.6058	0.2407
H(28)	0.0130	0.2960	0.2314	HR(35)	0.7277	0.5155	0.1526
H(31)	−0.0096	0.0828	0.0496	HR(36)	0.5812	0.4420	0.1158
H(32)	0.0071	0.0972	0.2053	HR(42)	0.2813	0.5431	0.0502
H(33)	0.0413	0.1905	0.2876	HR(43)	0.1010	0.5722	−0.0841
H(34)	0.2198	0.2385	0.3349	HR(44)	−0.0458	0.4991	−0.1638
H(35)	0.3155	0.2558	0.2490	HR(45)	−0.0122	0.3969	−0.1092
H(36)	0.2913	0.2408	0.0909	HR(46)	0.1681	0.3677	0.0251

[a] The labels are the same as the carbon atoms to which they bond.

Table IV. Interatomic Distances and Angles (Supplement to Figure 2)[a]

Average COT Distances (Å) and Angles (deg)

	COT 1 [C(11)–C(18)]		COT 2 [C(21)–C(28)]		COT 3 [C(31)–C(38)]
C–C	1.393 (8)	C–C	1.399 (10)	C–C	1.390 (12)
C–C–C	134.3 (7)	C–C–C	134.3 (6)	C–C–C	133.6 (8)

Shortest interligand contacts in anion (Å)

COT 1–COT 3	
H(13)···H(38)	2.56
H(31)···C(14)	2.63
H(32)···C(17)	2.71
H(17)···H(32)	2.73
COT 1–COT 2	
H(18)···H(27)	2.22
H(12)···H(23)	2.52
H(12)···C(23)	2.53
H(11)···C(25)	2.58
H(18)···C(27)	2.59
COT 2–COT 3	
H(22)···H(37)	2.46
H(28)···H(33)	2.47
H(21)···C(35)	2.48
H(21)···C(36)	2.55
H(22)···C(37)	2.57
H(22)···H(38)	2.63

Cation distances (Å)

As–CR(11)	1.89 (2)
As–CR(21)	1.89 (2)
As–CR (31)	1.89 (2)
As–CR (41)	1.89 (1)
	1.89 (1)

Angles in cation (deg)

CR(11)–As–CR(21)	107.8 (7)
CR(11)–As–CR(31)	108.4 (6)
CR(11)–As–CR(41)	110.4 (6)
CR(21)–As–CR(31)	110.4 (5)
CR(21)–As–CR(41)	109.3 (7)
CR(31)–As–CR(41)	110.6 (6)
	109.5 (5)
As–CR(11)–CR(12)	120.2 (10)
As–CR(11)–CR(16)	119.7 (10)
As–CR(21)–CR(22)	120.8 (12)
As–CR(21)–CR(26)	119.2 (12)
As–CR(31)–CR(32)	120.5 (9)
As–CR(31)–CR(36)	119.5 (9)
As–CR(41)–CR(42)	120.5 (11)
As–CR(41)–CR(46)	119.5 (11)
	120.0 (2)

[a] The estimated error of the mean was calculated according to $[\sum_i (d_i - \overline{d})^2/n(n-1)]^{1/2}$ where d_i and $\overline{d}$ are the distance or angle and mean value, respectively.

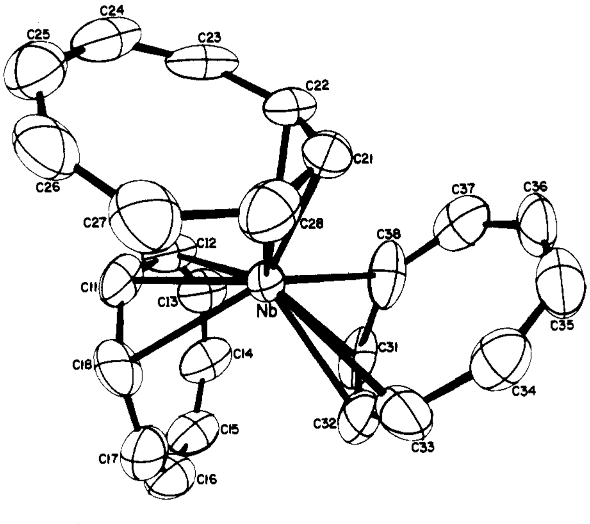


Figure 1. The structure of $[Nb(C_8H_8)_3]^-$.

109.5 (5) and 120.0 (2)°, respectively. Dihedral angles between phenyl rings vary from 60.6 to 114.9° (Table V). The shortest contacts between phenyl rings are 2.78 Å for C···H and 2.58 Å for H···H.

Intermolecular Contacts. Intermolecular contacts were examined carefully. The shortest are 2.61 Å for C···H[C(25)···HR(24)] and 2.34 Å for H···H[H(24)···HR(25)]. Intramolecular, interligand contacts in the anion are most important for COT carbon atoms closest to Nb, but intermolecular contacts predominate for more remote carbons. A stereoview of the unit cell (Figure 5) shows what is basically a sheet of cations in front of a sheet of anions.

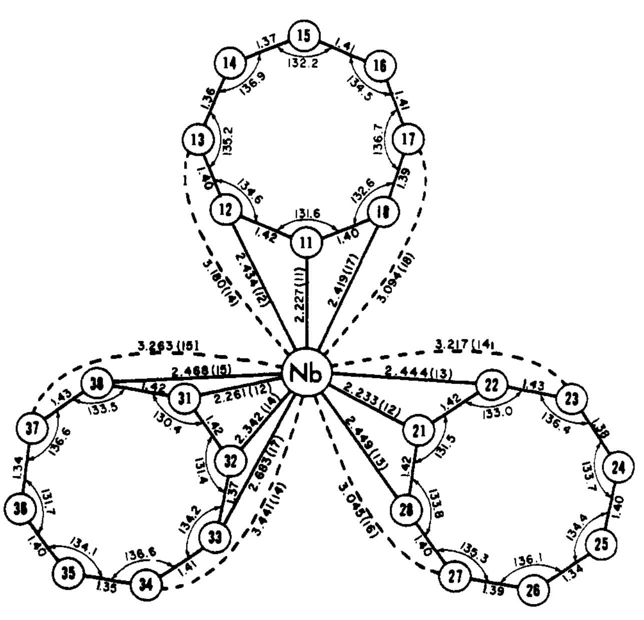


Figure 2. Idealized anion showing interatomic distances and angles.

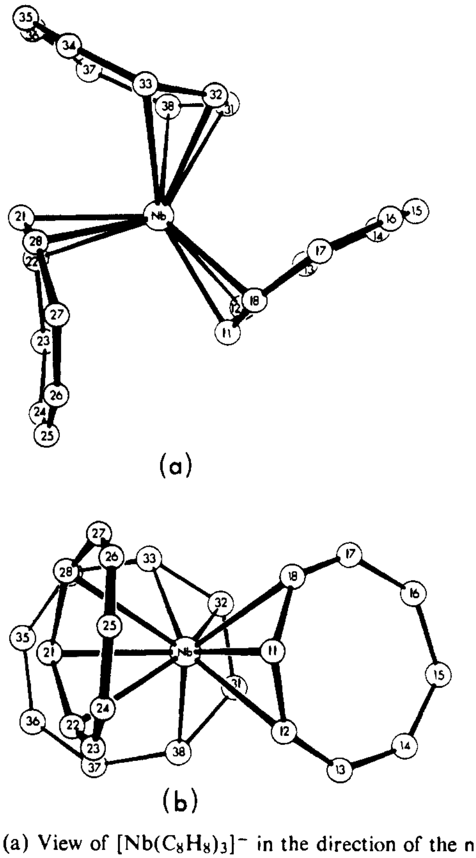
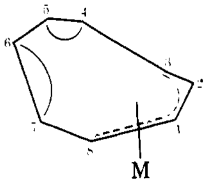


Figure 3. (a) View of $[Nb(C_8H_8)_3]^-$ in the direction of the normal to the idealized mirror plane. (b) View of $[Nb(C_8H_8)_3]^-$ showing the idealized mirror plane (horizontal) and the twist of COT 3.

Comparison with Other COT Structures. Mononuclear η^4-COT complexes without exception are based on a metal-butadiene type interaction (1) which has $C_s(m)$ point symmetry and is defined by planes C(1,2,3,8) and C(3-8).



1

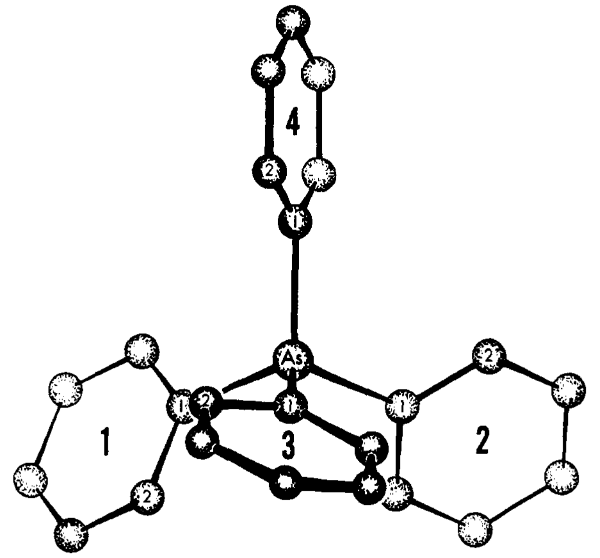


Figure 4. Structure of $[As(C_6H_5)_4]^+$.

Table V. Least-Squares Planes

Plane 1. $0.9131X + 0.0306Y + 0.4067Z + 2.575 = 0$
C(13) −0.003 C(15) −0.016 C(17) −0.004
C(14) 0.010 C(16) 0.012
Plane 2. $0.4074X + 0.8989Y + 0.1613Z - 5.291 = 0$
C(23) −0.014 C(25) 0.017 C(27) 0.022
C(24) 0.014 C(26) −0.038
Plane 3. $0.8159X - 0.4692Y + 0.3379Z + 1.104 = 0$
C(31) 0.014 C(33) 0.007
C(32) −0.015 C(38) −0.006
Plane 4. $-0.4317X + 0.8633Y - 0.2613Z - 3.002 = 0$
C(34) 0.002 C(36) 0.004
C(35) −0.004 C(37) −0.002

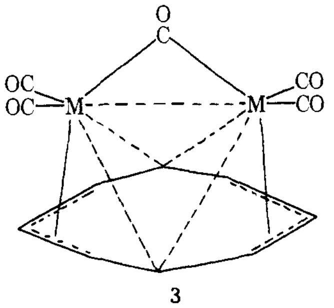
Dihedral Angles (deg)[a]

C(11), C(12), C(18) C(21), C(22), C(28)	120.8	C(23), C(24), C(26), C(27) C(24), C(25), C(26)	4.2
C(11), C(12), C(18) C(31), C(32), C(33), C(38)	120.9		
C(21), C(22), C(28) C(31), C(32), C(33), C(38)	118.0	C(31), C(32), C(33), C(38) C(33)–C(38)	26.4
C(11), C(12), C(18) C(12), C(13), C(17), C(18)	17.4	CR(11)–CR(16) CR(21)–CR(26)	80.5
C(12), C(13), C(17), C(18) C(13), C(14), C(16), C(17)	11.3	CR(11)–CR(16) CR(31)–CR(36)	65.6
C(13), C(14), C(16), C(17) C(14), C(15), C(16)	3.4	CR(11)–CR(16) CR(41)–CR(46)	114.9
C(21), C(22), C(28) C(22), C(23), C(27), C(28)	14.0	CR(21)–CR(26) CR(31)–CR(36)	93.4
C(22), C(23), C(27), C(28) C(23), C(24), C(26), C(27)	11.5	CR(21)–CR(26) CR(41)–CR(46)	60.6
		CR(31)–CR(36) CR(41)–CR(46)	67.1

[a] The angles are between the normals of the planes defined by the atoms in the first and second line.

Bond lengths in the butadiene fragment are nearly equal and single and double bonds alternate in the nonbonded portion of the molecule. The interplanar angle in COT 3, 153.6°, may be compared with that in $Fe(\eta^4\text{-}C_8H_8)(CO)_3$[20] (137.5°), $Ru(\eta^4\text{-}C_8H_8)(CO)_3$[21] (136.3°), $Fe(\eta^6\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)$[22] (147° for η^4-COT), and $Zr(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)(C_4H_8O)$[23] (159° for η^4-COT). The bond lengths within the butadiene fragment in COT 3 are nearly equal, but distances between the remaining, nonbonded COT carbons vary less than in group 8-η^4-COT complexes, suggesting π-delocalization over the COT 3 ligand to be more significant.[24] The smaller bond length distribution and larger interplanar angle in η^4-COT bound to Nb and Zr[23] may indicate a more aromatic character of the ring, but more evidence is needed to construct a convincing argument.

The *only* examples of η^3-COT ligands are in binuclear complexes,[25] $Fe_2(C_8H_8)(CO)_5$,[26] $Fe_2(C_8H_4(CH_3)_4)(CO)_5$,[27] and $Ru_3(C_8H_8)_2(CO)_4$,[28] where valence bond description **3** applies. The COT is "dish-shaped" in **3**, and the metals are bound on the *concave* side. Niobium is bound to the *convex* side of similarly shaped η^3-COT ligands in $[Nb(C_8H_8)_3]^-$. More complex allylic-type bonding in eight-membered carbocyclic ligands is found in $Ru_2(C_8H_8)(CO)_6$,[29] $Fe_2(C_8H_{10})(CO)_6$,[30] and $Fe_2(C_{12}H_{16})(CO)_5$.[31]



3

Nearly equivalent C-C distances in COT 1 (1.393 (8) av) and COT 2 (1.399 (10) av) indicate extensive π-delocalization over the η^3 rings also. The only questionable distance is C(25)-C(26) (1.338 (19) Å) which deviates statistically from the mean (1.399 (10) Å), 3σ; the ψ^2 test indicates the probability of this being part of a random distribution of equal bonds is 0.01.[32] In a purely statistical sense this difference is probably significant, but we attach little significance to it since local symmetry would favor a C(25)-C(26) distance comparable to C(24)-C(25) as well as perhaps C(14)-C(15) and C(15)-C(16). The large cation influence on the refinement precluded greater bond distance precision.

Bonding and Oxidation State in $[Nb(C_8H_8)_3]^-$. The COT 3 bonding may be described as a butadiene-type[33] with four ligand electrons distributed in molecular orbitals formed from two bonding ligand orbitals and two metal orbitals. At this time no simple bonding description can take π-delocalization into account.

Bonding to COT 1 and COT 2 is best described as an η^3-allyl type.[33] In metal-allyl complexes the C-C distances are usually equal and the M-C(central) distance is the same or slightly shorter than M-C(outer). In COT 1 and 2, M-C(central) is about 0.2 Å shorter than M-C(outer) due in part at least to the large C-C-C angle (131.5°), which places the terminal "allyl" carbons further apart than in true allyl complexes. Steric repulsions between ligands probably also contribute to a longer M-C(outer) distance. Bonding of an η^3-COT in this manner requires three COT electrons and one niobium electron in molecular orbitals formed from two ligand orbitals and two metal orbitals.

The bonding description therefore involves six nobium or-

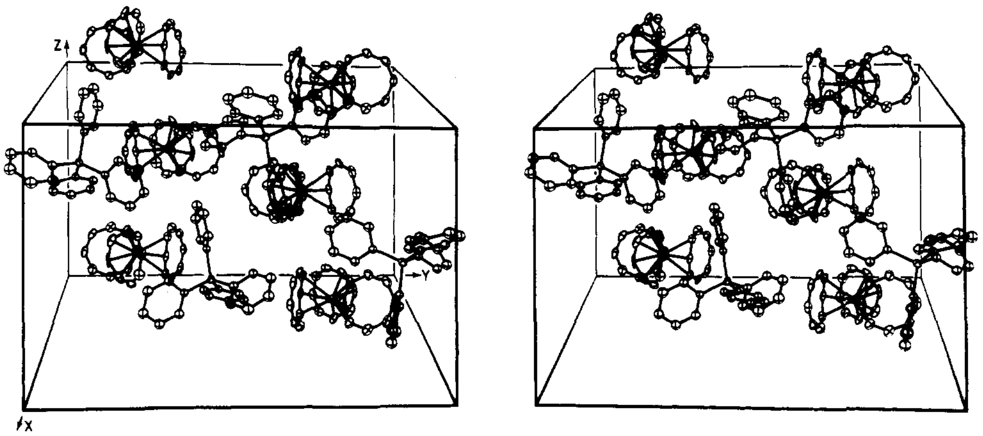


Figure 5. A stereoview of the packing in $[As(C_6H_5)_4][Nb(C_8H_8)_3]$.

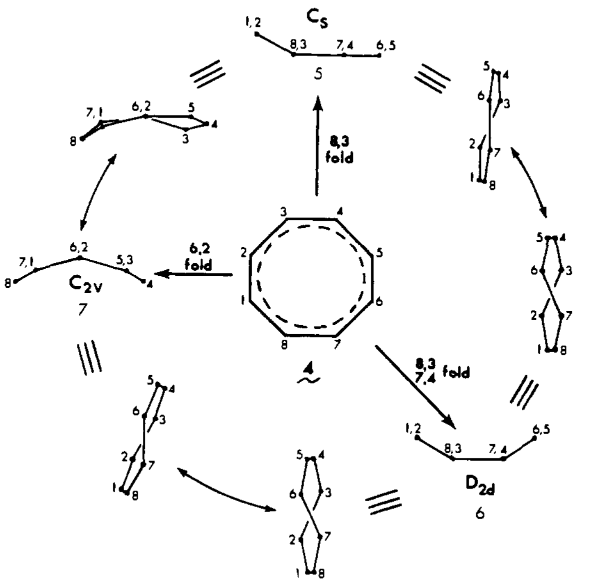


Figure 6. Cyclootatetraene conformations of neutral COT's in transition metal complexes.

bitals and six bonding ligand orbitals; two niobium electrons and ten ligand electrons form six Nb–COT bonds. Niobium is therefore formally Nb(+1) with 16 electrons in the valence shell. Several variations of this description are possible since the manner in which electrons are partitioned is not obvious. However, the extremes, Nb(−1) with three neutral ligands and Nb(+5) with three dianionic ligands, are least satisfactory.

Based on these structural data we favor an instantaneous solution structure with one η^4-COT and two η^3-COT's though a structure based on three η^3-COT's must be very close in energy; it is possible that the latter could even be the lowest energy structure in solution. Even a $[Nb(\eta^4\text{-}C_8H_8)_3]^-$ solution structure would seem plausible on steric grounds; possibly this does not occur because niobium prefers a lower electron density than that implied by the Nb(−1) formalism, a requirement the versatile COT ligands can readily accommodate.

Cyclooctatetraene Conformations. On the surface the common COT ligand conformations appear varied and not closely related. However, except for "tub" η^4-COT, all are closely related, a fact which warrants some discussion.

Only three basic types of conformations are accessible by minor bending vibrations from the planar conformation. These are closely related and readily interconvertible (see Figure 6). The basic conformations are $C_s(m)$, $D_{2d}(\bar{4}2m)$, and $C_{2v}(mm)$, **5**, **6**, and **7**, respectively, which are easily derived from **4**. Most importantly, the three are extremely close in terms of atom movement. To illustrate, we show alternate views for each; the equivalence signs identify different views of the same conformation. On the outer circle one conformation is obtained from another by small movements akin to minor bending modes. Actually, a near continuum of closely related conformations is possible especially where packing forces might stabilize lower symmetry conformations.

All conformations appear quite similar energetically and the particular one adopted will depend primarily on the metal's (or metals') electronic and steric requirements. For example, COT 3 as well as all the known η^4-bonded COT's (vide supra) would bond to 1, 2, 3, and 8 of **5**. Also COT's in **5** could act as six electron donors using atoms 3–8 for bonding; this happens in $Mo(\eta^6\text{-}C_8H_8)(CO)_3$,[34] $Cr(\eta^6\text{-}C_8H_8)(CO)_3$,[35] and $Fe(\eta^4\text{-}C_8H_8)(\eta^6\text{-}C_8H_8)$.[22] COT 1 and COT 2 in $[Nb(C_8H_8)_3]^-$, as well as the binuclear metal carbonyl complexes, use conformation **7**. Finally, the unusual η^4-COT in $[Ti(\eta^8\text{-}C_8H_8)]_2(\eta^4\text{-}C_8H_8)$ uses conformation **6**.[36]

Supplementary Material Available. A table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-6693.

References and Notes

(1) (a) The last general review in this area is by M. A. Bennett, *Advan. Organomet. Chem.*, **4**, 353 (1966); (b) see, for example, K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwelser, Jr., *J. Am. Chem. Soc.*, **95**, 8650 (1973); (c) see, for example, A. Streitwelser, Jr., U. Müller-Westerhoff, G. Sonnichsen, F. Mares, D. Morrell, K. O. Hodgson, and C. Harmon, *J. Am. Chem. Soc.*, **95**, 8644 (1973).

(2) F. A. Cotton, *Acc. Chem. Res.*, **1**, 257 (1968).

(3) R. P. M. Werner and H. E. Podall, *Chem. Ind. (London)*, 144 (1961).

(4) L. J. Guggenberger, *Inorg. Chem.*, **7**, 2260 (1968).

(5) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(6) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

(7) Computer programs used in addition to local programs were the Busing-Levy error function program ORFFE, the Johnson plotting program ORTEP, the least-squares program ORFLS, a copy of which was received from Dr. G. D. Stucky, and the Fourier program FOUR, a modification of a program written by Dr. C. J. Fritchie, Jr.

(8) See paragraph at end of paper regarding supplementary material.

(9) H. Breil and G. Wilke, *Angew. Chem.*, **78**, 942 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 898 (1966).

(10) R. R. Schrock and J. Lewis, *J. Am. Chem. Soc.*, **95**, 4102 (1973).

(11) The stability of $[\mathrm{Nb(CO)_6}]^-$ salts toward air and moisture follows a similar pattern; A. Davison, private communication.
(12) U. Klabunde, manuscript in preparation.
(13) R. R. Schrock, L. J. Guggenberger, and A. D. English, submitted for publication.
(14) N. I. Kirillova, A. I. Gusev, A. A. Pasynskii, and Yu. T. Struchkov, *J. Organomet. Chem.*, **63**, 311 (1973).
(15) L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973).
(16) L. J. Guggenberger, P. Meakin, and F. N. Tebbe, *J. Am. Chem. Soc.*, **96**, 5420 (1974).
(17) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 515 (1969); A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 739 (1969).
(18) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 107 (1969); A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 1365 (1968).
(19) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 294 (1969); A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 277 (1969).
(20) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).
(21) F. A. Cotton and R. Eiss, *J. Am. Chem. Soc.*, **91**, 6593 (1969).
(22) G. Allegra, A. Colombo, A. Immirzi, and I. W. Bassi, *J. Am. Chem. Soc.*, **90**, 4455 (1968).
(23) D. J. Brauer and C. Krüger, *J. Organomet. Chem.*, **42**, 129 (1972).
(24) In $\mathrm{Fe}(\eta^4\text{-}\mathrm{C_8H_8})(\mathrm{CO})_3$ π-delocalization extends at least to C(4) and C(7) (see **1**). Dickens and Lipscomb[20] found a π-overlap of 0.25 between C(3) and C(4), 0.16 between C(2) and C(3), and 0.33 between C(1) and C(2), yet the C(1)–C(2) and C(2)–C(3) distances are equivalent (1.42 Å). Bond lengths are probably an accurate measure of π-delocalization only in the nonbonded portion of the ring.
(25) For a review of binuclear complexes (two metals with a M–M bond bound to a common ligand) see A. N. Nesmeyanov, M. I. Rybinskaya, L. V. Rybin, and V. S. Kaganovich, *J. Organomet. Chem.*, **47**, 1 (1973).
(26) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 3158 (1966).
(27) F. A. Cotton and M. D. LaPrade, *J. Am. Chem. Soc.*, **90**, 2026 (1968).
(28) M. J. Bennett, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **90**, 6335 (1968).
(29) F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, **90**, 5412 (1968).
(30) F. A. Cotton and W. T. Edwards, *J. Am. Chem. Soc.*, **91**, 843 (1969).
(31) F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, **90**, 2031 (1968).
(32) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination", Macmillan, New York, N.Y., 1965, p 422.
(33) For pictures of η^4-butadiene and η^3-allyl ligand orbitals see M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen and Co., Ltd., London, 1968, pp 71 and 45, respectively.
(34) J. S. McKechnie and I. C. Paul, *J. Am. Chem. Soc.*, **88**, 5927 (1966).
(35) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).
(36) H. Dierks and H. Dietrich, *Acta Crystallogr., Sect. B*, **24**, 58 (1968).

---

[2]-Cryptates: Stability and Selectivity of Alkali and Alkaline-Earth Macrobicyclic Complexes

J. M. Lehn* and J. P. Sauvage

Contribution from the Institut Le Bel, Université Louis Pasteur, 67-Strasbourg, France.

Received March 6, 1975

Abstract: The stability constants of the [2]-cryptate inclusion complexes formed by the macrobicyclic ligands **1–6** with alkali and alkaline-earth cations have been measured. The origin of the stability sequences is discussed in terms of ligand structural features (topology, binding sites). The optimal alkali cryptates display much higher *stability* than any previously known complex. This high stability may be ascribed to the macrobicyclic topology of the ligands; this *cryptate effect* is several orders of magnitude larger than the macrocyclic effect with respect to an open chain chelating ligand. The selectivity of the complexes is also remarkable. Optimal fit of the cation into the intramolecular cavity agrees with the selectivity of ligands [2.1.1], [2.2.1], and [2.2.2] for $\mathrm{Li^+}$, $\mathrm{Na^+}$, and $\mathrm{K^+}$, respectively. The smaller ligands display *peak* selectivity whereas the larger ones display *plateau* selectivity, with only small differences in stability for $\mathrm{K^+}$, $\mathrm{Rb^+}$, and $\mathrm{Cs^+}$. Unusual selectivities are observed for the alkaline-earth cryptates, e.g., the high $\mathrm{Ca^{2+}/Mg^{2+}}$ and $\mathrm{Sr^{2+}}$, $\mathrm{Ba^{2+}/Ca^{2+}}$ ratios of ligands [2.2.1] and [2.2.2], respectively. Furthermore, $\mathrm{M^{2+}/M^+}$ selectivities are also of interest, especially the unique $\mathrm{Li^+} > \mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$ selectivity of ligand [2.1.1]. Changing from water to methanol solution generally leads to a marked increase in cryptate stability and selectivity. The results described provide strategies for the rational design of other specific ligands for metal cations.

The preferred complexation of a substrate S by a ligand L implies a *recognition* of S by L and its *selection* among the collection of possible substrates. Selectivity may be controlled by monitoring ligand structure, each specific feature representing an *information* bit. Information may be stored in: (1) the *topology* of the ligand, (2) its *binding* sites, (3) its *layer* properties. Medium and counterion are also expected to affect the stability and possibly the selectivity of the complex. A more detailed treatment of these general considerations is given in ref 2. The simplest substrate is a *spherical ion*, which, in addition to its simple shape, may also interact much more strongly with the ligand than a neutral species. The spherical *alkali* and *alkaline-earth metal cations* form complexes with various macrocyclic ligands of natural[3] or synthetic[4,5] origin.

Macrobicyclic ligands give 1/1 inclusion complexes with these cations, [2]-*cryptates*, in which the cation is contained inside the molecular cavity. We have recently described the formation and the structure of such cryptates[6] of the diazapolyoxamacrobicyclic ligands (*"cryptands"*) **1–6**.[7] We analyze here our results about the *stability* and *selectivity* of these complexes in terms of the ligand parameters mentioned above and discussed in more detail in previous reports.[2,6,7]

Since the cryptates are inclusion complexes, we shall formulate them by using the mathematical symbol of inclusion $\subset$, for instance $[\mathrm{K^+} \subset 2.2.2]$, ($\mathrm{K^+}$ included in ligand [2.2.2]) in order to distinguish them from addition complexes [L,S] (see ref 2, footnote 2). We also make use of the previously defined ligand nomenclature, [2.1.1], [2.2.1] etc., where the figures represent the number of oxygen atoms contained in each bridge of the bicyclic molecule.[2,6–8] All complexes of ligands **1–6** are macrobicyclic complexes, i.e., [2]-cryptates.[2]

Results

Determination of the Stability Constants. The complexation of a metal cation M^{n+} by a ligand L in a solvent S is represented by eq 1.

$$(\mathrm{L})_{\mathrm{solv}} + (\mathrm{M}^{n+}, m\mathrm{S}) \underset{k_\mathrm{d}}{\overset{k_\mathrm{f}}{\rightleftharpoons}} [\mathrm{L},\mathrm{M}^{n+}]_{\mathrm{solv}} + m\mathrm{S} \qquad (1)$$

where k_f and k_d are respectively the rates of formation and