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Ground States of Molecules. 52.¹ A MNDO SCF-MO Study of the Coordination of Beryllium-Indenyl and -Fluorenyl Complexes

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MNDO SCF-MO calculations have been carried out for the "half-sandwich" complexes formed between mono- and dibenzocyclopentadienyl anions (indenyl and fluorenyl, respectively) and BeH^+ or $BeCl^+$. Three stable isomers were located for the indenyl complexes, the calculated energies increasing with the coordination $\eta^1 > \eta^5 > \eta^6$. For the fluorenyl/ BeH system, no minimum corresponding to an η^5 isomer could be located, and the $9-\eta^1$ species was again lower in energy than the η^6 isomer. The calculated structure of the latter compound showed interesting similarities with the observed crystal structure of $(\eta^5\text{-cyclopentadienyl})(\eta^6\text{-fluorenyl})\text{iron}$.

Introduction

While an immense amount of work has been carried out on "sandwich" and "half-sandwich" complexes of transition metals, and while many of these compounds are of major technological interest and importance, few quantitative theoretical treatments of them are yet available.² Even the simplest compounds of this class contain too many electrons to be treated adequately by current ab initio procedures, particularly since the R-H (Roothaan-Hall³) method is known to be unsatisfactory for nonclassical species of this type if a minimum orbital basis set is used. Conventional semiempirical methods (EH, CNDO, INDO) are quite unsuitable for quantitative studies, while MINDO/3⁴ or the more recently developed MNDO⁵ have not yet been parametrized for transition metals, or indeed for compounds where d AO's are involved in bonding. There is, however, one metal which can form π complexes which contain only a few electrons and which has no d AO's in its valence shell, i.e., beryllium. Here ab initio calculations of fairly high quality are possible, although they are limited as yet to simple systems and are very rarely carried out with any geometry optimization because of the prohibitive cost it would entail. Now the group RBe, where R is a monofunctional ligand, resembles groups such as $Cr(CO)_3^-$ or $Mn(CO)_3$ (with vicinal carbonyls) in being a triple acceptor and in forming complexes of the type AX_3 with analogous geometries, the ligands X being equivalent and lying at the corners of an equilateral triangle. It therefore seems likely that half-sandwich compounds of beryllium may serve as reasonable models for analogous compounds of transition metals and that their study may therefore provide useful interim information until suitable treatments for the latter are developed.

MNDO has been parametrized for hydrogen and the second row elements Be, B, C, N, O, and $F^{5,7}$ and, as yet without d AOs, for Cl.⁸ Calculations for several hundred molecules of all kinds have given results in generally good agreement with experiment for heats of formation, molecular geometries, dipole moments, ionization energies, electron affinities,^{9a} and mo-

lecular vibration frequencies.^{9b} The energies calculated for beryllium compounds are less easily tested because of the lack of thermochemical data for these species in the gas phase. Other properties, however, agree with experiment, and the energies and geometries calculated by MNDO for smaller molecules containing beryllium are similar to those obtained by ab initio calculations.⁷ Thus, the most stable forms of cyclopentadienylberyllium hydride and acetylide were correctly^{10,11} predicted to involve bonding of the metal to the face of the ring, although σ -bonded isomers were calculated to be stable by MNDO and about 10 kcal/mol higher in energy.⁷

Regarding the accuracy and reliability of MNDO in general, an interesting indication is provided by reference to a recent paper by Halgren et al.¹² in which they compare a wide variety of procedures other than ours. For the group of reactions they use as a criterion, the average error in heats of formation calculated by MNDO is less than that given by any of the methods Halgren et al. considered, including an ab initio SCF-MO one using a basis set of double- ζ type. The average errors in the case of analogous minimum basis set procedures, or Lipscomb's PRDDO method, are three times greater than that from MNDO. In general, the errors in all molecular properties calculated by MNDO seem as a rule to be no greater than those given by ab initio methods using very large basis sets.¹⁹

Recently, the properties of mono- and dibenzocyclopentadienyl anions (indenyl, $C_9H_7^-$, and fluorenyl, $C_{13}H_9^-$, respectively) as ligands have attracted attention. The indenyl ligand normally forms complexes with transition-metal ions that have η^5 coordination,¹³ although σ -bonded indenyl complexes (e.g., of mercury¹⁴) are known, and coordination to the six-membered ring of the 1-H protonated ligand has been observed.¹⁵ Metal complexes of the fluorenyl ligand have recently been synthesized¹⁶ and appear to be pentacoordinated,¹⁶ although isomers with η^6 coordination have recently been reported (i.e., $Mn(\eta^6-C_{13}H_9)(CO)_3$ ^{17a} or $Fe(\eta^5-C_9H_7)(\eta^6-C_{13}H_9)$ ^{17b}). In the case of the manganese complex, slow

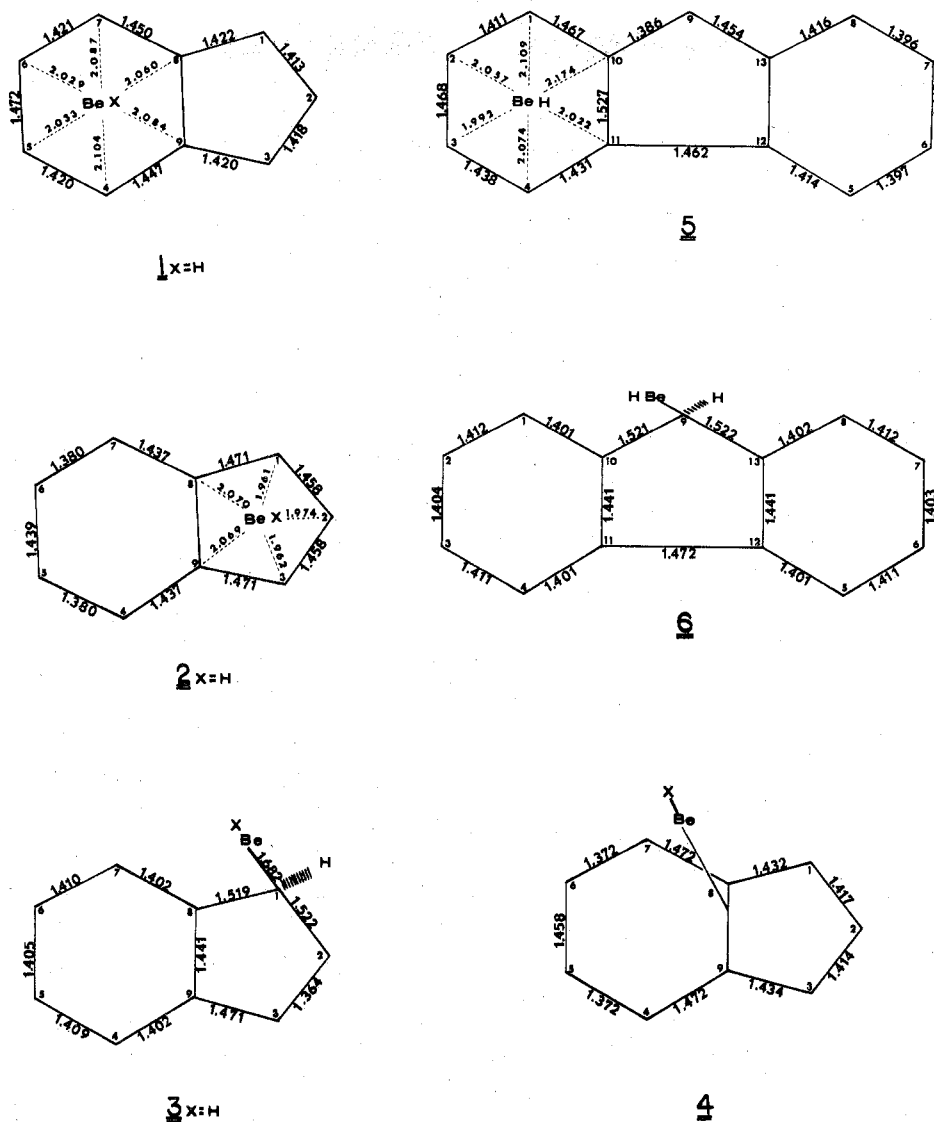


Figure 1. Calculated carbon-carbon bond lengths (Å) for 1-6 (X = H). Deviations from C_2 symmetry for 1-2, 5-6 are within the tolerances of the geometry optimization.

thermal isomerization to the more stable η^5 isomer was observed, whereas the iron complex could not be induced to rearrange.¹⁷

In this paper we report MNDO calculations for beryllium half-sandwich complexes with the indenyl and fluorenyl ligands.

Procedure

The MNDO procedure has been described in detail.⁵ The calculations were carried out using the parameters previously recommended.^{5,7,8} All geometries were calculated by minimizing the energy with respect to all geometrical parameters, no assumptions of any kind being made. These optimizations were carried out by our standard Davidon-Fletcher-Powell procedure.^{5a} In one case the transition state for the interconversion of isomeric species was located, this being first found approximately by the usual reaction coordinate method and then refined by minimizing the scalar gradient of the energy.¹⁸

Results and Discussion

A. The Indenyl ($C_9H_7^-$) Ligand. Three stable isomers were located for the indenylberyllium hydride or chloride systems, corresponding to η^6 (1), η^5 (2), or η^1 (3) coordination. The calculated properties of 1-3 are given in Table I and the geometries of the carbon skeletons are shown in Figure 1. The transition state 4 for the isomerization of 1 to 2 was located, the metal atom residing almost directly over the central C(8)-C(9) bond. MNDO predicts 1 (X = H) to be 14.4

Table I. Calculated Properties of the Beryllium Complexes 1-6

compd	ΔH_f , kcal/mol	dipole moment, D	first ionization potential, eV
1, X = H	47.7	2.53	8.05
1, X = Cl	1.8	3.42	8.23
2, X = H	33.3	1.98	8.70
2, X = Cl	-13.1	3.46	8.84
3, X = H	30.4	0.50	8.61
3, X = Cl	-18.5	1.20	8.73
4, X = H	57.2	0.61	8.09
4, X = Cl	9.3	1.90	8.25
5	60.1	2.60	7.82
6	39.2	0.28	8.53

kcal/mol less stable than the η^5 isomer 2, although an appreciable barrier (9.5 kcal/mol) was found for the isomerization. The η^1 isomer (3) was the most stable, being 2.9 kcal/mol lower than 2 in energy. We have previously⁷ reported that MNDO predicts the η^1 isomer of cyclopentadienylberyllium hydride to be only 9.1 kcal/mol higher in energy than the η^5 isomer. There is no experimental estimate of this energy difference. However, since MNDO underestimates the stabilities of compounds in which a high degree of multicenter bonding is important (cf. certain carboranes^{5d} and boron hydrides^{5b}), it seems probable that the calculated energies of

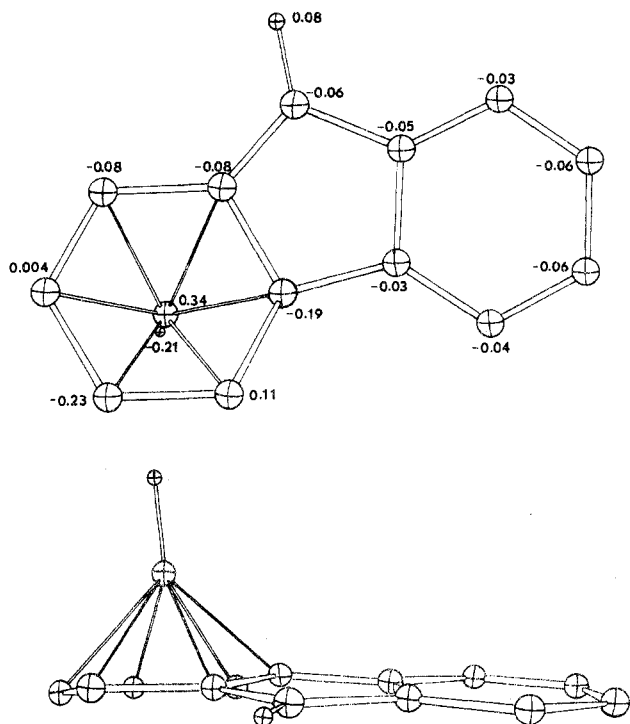


Figure 2. ORTEP plot of **5** showing the calculated MNDO charge distributions. Illustrated beneath is a projection showing the deviation from planarity of the ligand. Hydrogen atoms (except at C(9) and Be) are not shown for clarity.

1 and **2** are too high with respect to **3**. The relative energies of **1** and **2** are probably predicted more reliably and are certainly in accord with the observed coordination in compounds such as bis(indenyl)iron.¹³

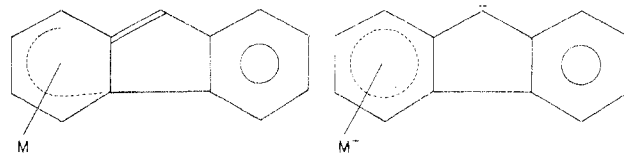
The calculated geometries of **1** and **2** show the ligand to be slightly nonplanar. In **1** (X = H) the metal-to-carbon distances are almost constant (Figure 1) and the central C(8)–C(9) bond is rather long (1.53 Å). In **2** (X = H) the metal-to-carbon distances showed more variation (Be–C (C(8), C(9)), 2.07 Å; Be–C (C(2), C(3)), 1.96 Å). Substitution of the beryllium hydride by beryllium chloride (**1–4**, X = Cl) showed little effect on the relative stabilities and geometries of the η^5 and η^6 isomers, although the barrier to interconversion (7.1 kcal/mol) was found to be reduced slightly.²⁰

B. The Fluorenyl (C₁₃H₉[−]) Ligand. Analogous structures were investigated for the fluorenyl system. The η^6 isomer **5** was found to be stable, but no minimum corresponding to η^5 coordination could be located, all geometry optimizations resulting in location of the 9- η^1 isomer **6**. This species was calculated to be 20.9 kcal/mol lower than **5** in energy (Table I). For the reason given above, it seems likely that MNDO is underestimating the energy of **5** with respect to **6**. These results suggest that it may be possible to isolate two isomeric forms of this complex under suitable conditions. We did not, however, calculate the energy barrier separating the two isomers.

The geometries of the carbon skeletons of **5** and **6** are shown in Figure 1. Comparison of the calculated geometry of **5** with the recently reported X-ray structure of Fe(η^6 -C₁₃H₉)(η^5 -C₅H₅)¹⁷ shows some interesting similarities. In both cases, the longest metal to fluorenyl ring distance is to C(10) (2.316 Å for Fe, 2.174 Å for Be) and the shortest is to C(3) (2.039 Å for Fe, 1.992 Å for Be). A large difference was also found between the C(10)–C(9) and C(9)–C(13) bond lengths (1.384 and 1.424 Å for Fe; 1.386 and 1.454 Å for Be).

The atomic charge distribution calculated for **5** is shown in Figure 2. There is surprisingly little negative charge on C(9) (−0.06 e) and a large amount of charge alternation on

the ring bearing the metal atom. This tends to suggest that of the two valence representations of the fluorenyl ligand suggested by Johnson and Treichel,¹⁷ the cyclohexadienyl one is the most appropriate for the beryllium complex. On this basis, by analogy with the relatively low observed nucleophilicity of the C(9) atom in Mn(η^6 -C₁₃H₉)(CO)₃,¹⁷ one might expect this carbon atom in the beryllium complex to exhibit relatively modest basic or nucleophilic properties.



Conclusions

The calculations reported here suggest that as yet unreported half-sandwich complexes of beryllium hydride or chloride with the indenyl or fluorenyl ligands may exist in two or more isomeric forms, differing only in the coordination of the metal atom. Studies of beryllium complexes may also be of use in predicting the structures and reactivities of similar transition-metal complexes.

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Registry No. **1**, X = H, 68682-96-2; **1**, X = Cl, 68682-97-3; **2**, X = H, 68682-98-4; **2**, X = Cl, 68682-99-5; **3**, X = H, 68646-41-3; **3**, X = Cl, 68646-42-4; **5**, 68683-00-1; **6**, 68646-43-5.

Supplementary Material Available: Optimized Cartesian coordinates for **1–6** (5 pages). Ordering information is given on any current masthead page.

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Fluorescence Spectra and Lifetime Measurements of Aqueous Solutions of Europium Nitrate and Perchlorate

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The relative intensities of the ${}^5D_0 \rightarrow {}^7F_J$ and ${}^5D_1 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) transitions and the fluorescence lifetime of aqueous solutions of europium(III) perchlorate and nitrate are reported. For perchlorate solutions, these data are independent of both the salt (0.01–1 M) and the total perchlorate ($[ClO_4^-]/[Eu^{3+}]$ between 3 and 28) concentrations, reflecting an outer-sphere-type interaction between Eu^{3+} and ClO_4^- . A different situation is met for nitrate solutions: τ varies from 110 μs (salt concentration 0.004 M) to 121 μs (1 M) and to 138 μs ($[ClO_4^-]/[Eu^{3+}] = 53$), reflecting an inner-sphere interaction. The lifetime of $[Eu(NO_3)(H_2O)_n]^{2+}$ amounts to 159 μs and its formation constant is found to be $0.3 \pm 0.1 M^{-1}$ in a 0.1 M aqueous solution of $Eu(NO_3)_3$.

The interaction between lanthanoid ions Ln(III) and NO_3^- in aqueous solutions has been studied by different techniques.^{1–12} If the existence of inner-sphere complexes has been unambiguously demonstrated,^{3,5,8,11,12} the overall Ln(III)/ NO_3^- interaction probably results in the formation of both inner- and outer-sphere complexes.^{2,6,7} Attempts have been made to calculate the corresponding association constants.^{1,4,6–9} Outer-sphere complexation or ion-pair formation between ClO_4^- and Ln(III) is known,^{1,13,14} but the existence of inner-sphere complexes is doubtful and remains controversial.^{10,11,14,15} We are currently involved in a thorough investigation of the Ln(III) first coordination sphere in solids^{16,17} and in both aqueous and strictly anhydrous solutions by means of spectrophotometric, fluorescence, conductometric, IR, and Raman measurements. A recent note in this journal about complex formation in dilute aqueous solutions of europium perchlorate¹⁸ urges us to present some of the results that we have obtained from fluorescence and conductometric measurements of aqueous solutions of europium nitrate and perchlorate.

Experimental Section

$Eu(NO_3)_3 \cdot 6H_2O$ and $Eu(ClO_4)_3 \cdot 7H_2O$ were prepared from 99.99% Eu_2O_3 (Glucydur) and reagent grade acids (Merck). The europium salts were analyzed as described in ref 19. Solutions of Eu(III) were prepared using triply distilled water; the exact Eu(III) concentration was checked by complexometric titration with EDTA. The excess of NO_3^- or ClO_4^- was obtained by adding $(CH_3)_4NNO_3$ (Fluka, puriss) or $NaClO_4 \cdot H_2O$ (Merck). Degassing the solutions with N_2 or Ar did not influence the fluorescence lifetimes.

Fluorescence spectra were excited at 394 nm (${}^7F_0 \rightarrow {}^5L_6$) by a Zeiss 450-W Xenon pressure lamp coupled with a Zeiss M-20 monochromator (band-pass used: 4 nm). Control runs of some spectra were recorded using excitation at 465 nm (${}^7F_0 \rightarrow {}^5D_2$). The samples were put into 1-cm Spectrosil cells which were placed into a high-sensitivity, specially designed probe holder. The fluorescence light was analyzed at 90° with a 0.5-m Czerny-Turner monochromator from Spex Industries (Model 1870) equipped with a 1200 lines/mm grating blazed at 26°45', with a maximum resolution of 0.02 nm. Light intensity was measured by a RCA 31034c photomultiplier with a cooled Ga-As photocathode (S-20 response, dark count <15 counts/s at 1920 V and -20 °C) coupled to an Ortec photon counting unit. The relative intensities of the ${}^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions were obtained

by direct planimetry of the spectra since the response of the spectrofluorimeter is almost constant between 570 and 630 nm; contributions from the 5D_1 level fluorescence were evaluated and subtracted.

Fluorescence lifetimes were measured using two different setups. (i) The solutions were excited at 592.5 nm (${}^7F_1 \rightarrow {}^5D_0$) by a flash lamp pumped CMX-4 dye laser from Chromatix containing rhodamine 6G. The pulse length was 1.3 μs with an average power of 30–40 mW at a repetition rate of 10 pulses/s (pps). Light from the ${}^5D_0 \rightarrow {}^7F_4$ transition at 695.0 nm was analyzed as above, except that the output of the PM was connected ($\tau_{RC} < 2 \mu s$) to a Bruker BC-104 transient recorder coupled to a DL-4000 signal averager from Datalab equipped with a DL-450 microprocessor. The lifetimes were calculated over at least 3 lifetimes after 512 or 1024 accumulations: $\tau = 1/s$, s being the slope of $\ln I = f(t)$. (ii) The Eu(III) ions were excited at ~395 nm (${}^7F_0 \rightarrow {}^5L_6$) by a Xe flash lamp coupled to the M-20 monochromator. The pulse length was 2–5 μs with an estimated average power of 0.5 mW at 1 pps. The lifetimes obtained measuring the decay of the ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, and ${}^5D_0 \rightarrow {}^7F_4$ transitions were identical with each other and to the lifetimes determined by method (i). All the data reported in the tables are averages of 2–6 determinations on at least two independent samples.

Conductometric measurements were performed at 25.6 ± 0.1 °C using an E-365 conductimeter from Metrohm.

Results and Discussion

The molar conductivity λ_M of 2×10^{-4} M aqueous solutions of $Eu(NO_3)_3$ and $Eu(ClO_4)_3$ are 423 and 435 $\Omega^{-1} mol^{-1} cm^{-1}$, respectively. These data are in good agreement with the known values for the other lanthanoids,²⁰ which means that both salts are 3:1 electrolytes. When the concentration of the solutions is increased, λ_M decreases and amounts to 336 for 10^{-2} M $Eu(ClO_4)_3$ and 339 for 4×10^{-3} M $Eu(NO_3)_3$, reflecting the formation of outer- and possibly inner-sphere complexes.

Fluorescence spectra and fluorescence lifetimes are very sensitive to the first solvation sphere of the Eu(III) ion and they can be used to study the weak interaction between Eu(III) and different anions. Upon excitation to the 5L_6 level, the Eu(III) ions fluoresce mainly from the 5D_0 (92–94% of the total fluorescence intensity of europium perchlorate solutions) and from the 5D_1 (6–8%) excited states. Weak fluorescence from the 5D_2 level (<0.2%) is also observed. The fluorescence spectrum of europium perchlorate (see Figures 1 and 2 and Table I) shows that the aquo ion probably possesses a center