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Molecular Orbital Calculations on Transition-Metal Complexes. 22.[1] Bis(borabenzene) Compounds of the 3d Series

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INDO–SCF molecular orbital calculations have been carried out for the bis(borabenzene) $M(C_5H_5BR)_2$ (R = H, M = Cr, Mn, Fe, Co; R = CH_3, M = Fe, Co) complexes of the 3d series. The major contribution to the d-orbital splitting is found to arise from the interaction between the ligand π orbitals and the metal $e_1(d_{xz},d_{yz})$ orbitals, which become strongly antibonding, but the ligand σ orbitals play a significant role in the bonding and are substantially mixed with the metal $e_2(d_{x^2-y^2},d_{xy})$ and $a_1(d_{z^2})$ levels. The ordering of the mainly metal 3d levels corresponds to the one-electron energy sequence $d_{x^2-y^2} \sim d_{xy} < d_{z^2} \ll d_{xz} \sim d_{yz}$, similar to that observed for the metallocenes, and the calculated splittings for the Fe derivative agree closely with those deduced from the electronic spectrum of bis(1-methylborabenzene)iron via the ligand field model. As for ferrocene, however, the SCF orbital energies in $Fe(C_5H_5BH)_2$ indicate the sequence $d_{z^2} < d_{x^2-y^2} \sim d_{xy}$, although electron loss from all three levels is calculated, via the appropriate state energies for the corresponding cation, to be almost equienergetic. For the Co derivatives the splitting of the formerly degenerate $e_1(d_{xz},d_{yz})$ level, due to the ring heteroatoms, is found to be quite small ($\sim$3000 cm^{-1} or less), contrary to a recent interpretation of ESR data for bis(1-phenylborabenzene)cobalt, and a ground-state configuration $[(d_{x^2-y^2})^2(d_{xy})^2(d_{z^2})^2(d_{xz} \text{ or } d_{yz})^1]$, $^2E_1$, is always more stable than $[(d_{x^2-y^2})^2(d_{xy})^2(d_{xy} \text{ or } d_{yz})^2(d_{z^2})^1]$. Moreover, simple ligand field considerations enable the ESR data to be reconciled with this conclusion. For the Cr system an effectively $^3E_2(e_2{}^3a_1)$ rather than a $^3A_2(e_2{}^2a_1{}^2)$ state is calculated to lie lower, with only a small splitting of the e_2 level, in accordance with the orbital contribution to the magnetic moment observed for the 1-methyl and 1-phenyl derivatives. Symmetrical $Mn(C_5H_5BR)_2$ species are as yet unknown, but the results suggest that the $^2E_2(e_2{}^3a_1{}^2)$ and $^2A_1$ $(e_2{}^4a_1)$ states should lie very close together, with the $^6A_1(e_2{}^2a_1e_1{}^2)$ level slightly higher. The molecular orbital compositions for the $M(C_5H_5BR)_2$ species show the borabenzene ligand to be intermediate between Cp (π-C_5H_5) and Bz (π-C_6H_6) in its bonding characteristics, but with an appreciably greater involvement of the ligand σ levels.

Introduction

The first bis(borabenzene) derivatives of the transition metals were obtained by Herberich et al.[2] in 1971 when the cobalt compounds $Co(C_5H_5BR)_2$ (R = CH_3, C_6H_5) were prepared by ring expansion of cobaltocene, $CoCp_2$, with substituted boron chlorides, $RBCl_2$. Later the corresponding iron compounds were synthesized by treatment of the cobalt compounds with iron carbonyls and subsequent pyrolysis,[3] but a more general synthetic route was developed by Ashe and his co-workers[4,5] in which 1-substituted borabenzene anion salts were allowed to react with appropriate metal halides, and this technique has recently permitted the preparation of the analogous chromium species.[6]

This latter synthetic approach in fact underlines the similarities between the borabenzene complexes and the corresponding metallocene compounds since in both cases the ligands may be regarded as formally negatively charged moieties, $[C_6H_5BR]^-$ and $[C_5H_5]^-$, respectively, and substantial evidence has been accumulating that both ligands behave as 6π-electron systems.[5,7] This reasoning is supported by the results of X-ray crystallographic studies[8] of the 1-methyl and 1-methoxy bis(borabenzene)cobalt compounds which show the ligand rings to be essentially planar and indicate genuine sandwich structures in both cases, with the boron atoms of the rings disposed trans to one another. The overall point symmetry of such systems cannot therefore strictly be higher than C_{2h}, but by analogy with substituted metallocenes it might be anticipated that many properties of the bis(borabenzene) species could satisfactorily be treated with the assumption of approximately pseudoaxial ($C_{\infty v}$) symmetry. In this way, using the ligand field theory developed[9] for such sandwich species, we have estimated the one-electron splitting parameters for the d orbitals for the $Fe(C_5H_5BR)_2$ systems from the recorded electronic spectra,[5] leading (vide infra) to the sequence $e_2 < a_1 \ll e_1$, with the quantities ΔE_1 and ΔE_2 ($=H_{e_1}{}^{\text{core}} - H_{a_1}{}^{\text{core}}$ and $H_{a_1}{}^{\text{core}} - H_{e_2}{}^{\text{core}}$, respectively) actually slightly larger than for the corresponding metallocene, ferrocene.

On the other hand, an ESR study of the bis(1-phenylborabenzene)cobalt complex has recently been reported by Herberich, Lund, and Raynor,[10] in which the conclusion was reached that the splitting of the formerly degenerate $e_1(d_{xz},d_{yz})$ level is substantial and sufficient to lead to one component of this level becoming lower in energy than the $a_1(d_z{}^2)$ orbital, thereby locating the odd electron in this latter, non-orbitally-degenerate level. Since our ligand field estimates suggested that for the bis(borabenzene) complexes ΔE_1 should be of the order of 25 000 cm^{-1}, these viewpoints are clearly in conflict, and we have accordingly carried out full basis set INDO–SCF calculations for a number of transition-metal–bis(borabenzene) systems in an attempt to resolve this disagreement. In the course of this study we have been able to obtain more information regarding the behavior of the C_5H_5BR ligand in sandwich species and to make comparisons with the related metallocene, $M(C_5H_5)_2$, and bis(arene), $M(C_6H_6)_2$, systems. Furthermore, we have shown that many of the experimental data for the bis(borabenzene) systems, including the ESR results, are consistent both with a simple ligand field model[9] and with the results of our molecular orbital calculations.

Method

The all valence electron INDO–SCF–MO method developed in these laboratories[11] was used throughout the calculations. The basis set employed spanned the metal 3d, 4s, and 4p, the carbon and boron 2s and 2p, and the hydrogen 1s orbitals. The appropriate orbital parameters have previously been listed.[11] In all the computations total energies were iterated until the results of successive cycles differed by less than 0.001 au, so that the results are therefore not significant to better than 0.025 eV or 200 cm^{-1}.

The geometry adopted for the borabenzene rings was based upon that reported by Huttner, Krieg, and Gartzke[8] for bis(1-methylborabenzene)cobalt, and in all cases the boron atoms of the two rings were taken to lie in the trans conformation, the axes being labeled as shown in Figure 1. The X-ray data indicate, however, that the metal atom is not in fact symmetrically placed with respect to the borabenzene rings but is actually displaced slightly away from the boron ends of the rings. Consequently there are effectively two independent distance variables of which account should be taken in any calculations: first, the distance from the metal atom to the plane of the borabenzene ring and second, what may

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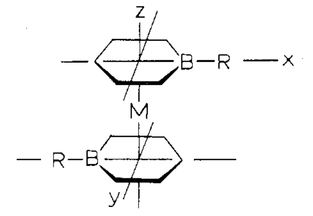

Figure 1. Notation of axes for bis(borabenzene)–metal systems.

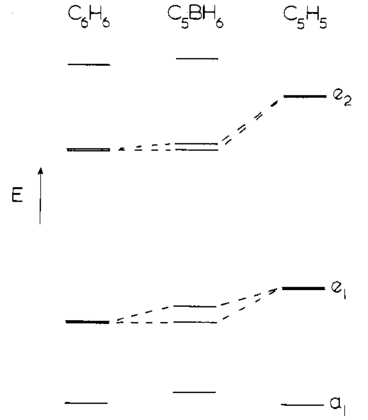

Figure 2. π-Type molecular orbitals of the benzene, borabenzene, and cyclopentadienyl ligands.

be regarded as a slipping motion of the two borabenzene rings in contrary directions ($+x$ and $-x$, respectively). The former, the metal–ring plane distance, is thus equivalent to the z coordinate of the ring atoms and the latter, the slip distance, may be represented by the x coordinate of the C_4 ring atom. It should be noted that the X-ray data actually indicated a very small deviation of the borabenzene rings from planarity, but in order to preserve the simplicity of the σ–π subdivision of the ring orbitals we used throughout a planar ring structure which was as nearly as possible equivalent to the crystallographic result.

For the cobalt systems the metal–ring plane and slip distances were independently varied over the ranges 1.45–1.65 Å and 1.11–1.61 Å, respectively, for all of the possible ground-state configurations, the values 1.55 and 1.31 Å being finally adopted. For the other 3d complexes the slip distance was assumed to be the same but, by analogy with the corresponding metallocenes, the metal–ring plane distances of 1.60, 1.60, and 1.50 Å, respectively, were taken for the Cr, Mn, and Fe compounds.

Results and Discussion

General Considerations. It has been customary to regard the bonding in transition-metal sandwich species as deriving dominantly from the interaction between the metal 3d orbitals and the π orbitals of the ligand rings: in fact, we have recently demonstrated quantitatively, by calculation of the appropriate metal–ring bond orders,[1] that this assumption is rather well founded for 3d systems involving π-C_5H_5 (Cp), π-C_6H_6 (Bz), and π-C_7H_7 (Ch) ligands. Furthermore, it is well-known that the one-electron energies of the ligand π-orbital combinations of e (twofold degenerate) symmetry decrease progressively with increasing ring size,[12] as shown in Figure 2. Thus, on this simple picture, the interaction of the ligand e_1 levels with the metal 3d orbitals diminishes with increasing ring size, leading to the dominantly metal $e_1(d_{xz},d_{yz})$ orbitals being less antibonding, while conversely the $e_2(d_{x^2-y^2},d_{xy})$ interaction becomes stronger and the resultant dominantly metal 3d levels more bonding in character. The energy of the a_1 ligand π combination is not however, in this approximation, changed by variation of the ring size, and the metal $a_1(d_{z^2})$ level remains effectively nonbonding, largely due to unfavorable overlap.[1]

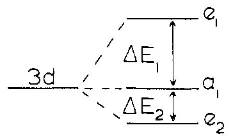

Figure 3. Ligand field splitting of the d orbitals in pseudoaxial symmetry.

The one-electron splitting of the 3d levels thus resulting may be expressed in terms of the quantities ΔE_1 and ΔE_2 as shown in Figure 3, where these are respectively equal to the differences in the H^{core} terms of the e_1 and a_1 levels and of the a_1 and e_2 levels. On a simple ligand field model[9] the Cp ligand may be regarded as a 6π-electron system, $[C_5H_5]^-$, so that ferrocene, $FeCp_2$, regarded as $Fe^{2+},2Cp^-$, would represent a d^6 system with filled, mainly metal, e_2 and a_1 levels; similarly $CrBz_2$, regarded as $Cr^0,2Bz^0$, would also constitute a d^6 configuration.

However, the replacement of a carbon atom of the benzene ligand by a boron atom, giving the C_5H_5BR ligand, also leads to systems in which the metal atom may formally be treated as M^{2+}, so that the iron compounds, regarded as $Fe^{2+},2$-$[C_5H_5BR]^-$, are also d^6 systems and clearly analogous to ferrocene. Moreover, the introduction into the benzene ring of the more electropositive heteroatom, boron, will lift the degeneracies of the twofold degenerate e_1 and e_2 π-ligand combinations (Figure 2), raising one component in energy; thus qualitatively we should expect that the e_1 interaction in borabenzene species might be weaker than for MCp_2 systems but stronger than for MBz_2 compounds, while for the e_2 interaction the bis(borabenzene) complexes should show the opposite behavior, being more strongly involved than in MCp_2 species but less so than for MBz_2 compounds. Finally, it might be anticipated that since the ligand a_1 level is raised in energy relative to both the Cp and Bz systems, it should be somewhat more involved in the bonding than in either the metallocene or the bis(benzene) series.

We shall therefore, in discussing our results for the individual systems studied, examine the accuracy of these predictions, bearing in mind where appropriate the distinction between one-electron energies and SCF orbital energies. In addition, more significant involvement of the σ frameworks of the ligand rings might be anticiptated since the insertion of the more electropositive boron atom will lift the energies of the ligand σ combinations as well as those of the π-orbital levels.

Bis(borabenzene)–Cobalt Systems. On the simple picture outlined above the $Co(C_5H_5BR)_2$ systems should constitute formally Co^{II}, d^7 species for which a $^2E_1(e_2{}^4a_1{}^2e_1)$ ground state would be expected. In addition, by analogy with complexes such as the 1,1′-disubstituted metallocenes and the various methyl-substituted bis(benzene) systems, relatively modest splittings of the e_1 and e_2 levels should ensue, leading to situations approximating quite closely to pseudoaxial symmetry. However, the interpretation of the ESR spectrum of bis(1-phenylborabenzene)cobalt in toluene–ether solution at 77 K, put forward by Herberich, Lund, and Raynor,[10] postulated a very substantial splitting of the e_1, mainly metal 3d level, such that the lower component thereof actually fell below the $a_1(3d_{z^2})$ level, thereby producing a $[(d_{x^2-y^2})^2(d_{xy})^2(d_{xz}$ or $d_{yz})^2(d_{z^2})^1]$ ground-state configuration. We therefore performed calculations for the parent system, $Co(C_5H_5BH)_2$, initially taking bond distances corresponding to the crystallographic values, in order to ascertain which d-orbital configuration corresponded to the lowest energy situation. With our first choice of values—metal–ring plane = 1.65 Å and slip distance = 1.31 Å—the $[(d_{x^2-y^2})^2(d_{xy})^2(d_{z^2})^2(d_{yz})^1]$ configuration (configuration A) lay lowest, some 2000 cm^{-1} (0.25 eV)

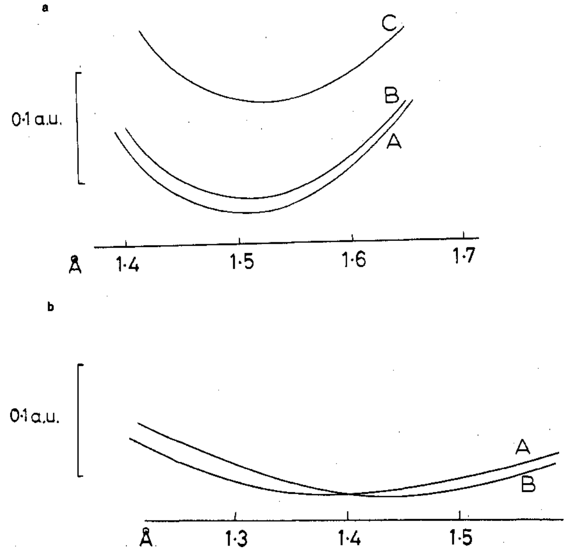

Figure 4. (a) Variation of total energy of $Co(C_5H_5BH)_2$ with metal–ring distance—slip distance 1.31 Å. (b) Variation of total energy of $Co(C_5H_5BH)_2$ with slip distance—metal–ring distance 1.55 Å.

below configuration B ($[(d_{x^2-y^2})^2(d_{xy})^2(d_{z^2})^2(d_{xz})^1]$), and no less than 17 350 cm^{-1} (2.15 eV) below $[(d_{x^2-y^2})^2(d_{xy})^2(d_{xz})^2(d_{z^2})^1]$ (configuration C); moreover, the interchange of d_{yz} for d_{xz} in configuration C had no significant effect upon the energy separation. Consequently, we made a systematic study of the effect of the variation of the metal–ring plane distance and of the slip distance upon the relative energies of configurations A, B, and C, for the $Co(C_5H_5BH)_2$ system, but in all cases configuration C (with either d_{xz} or d_{yz} doubly occupied) was found to lie at appreciably higher energies—never less than 2 eV—than configurations A and B.

In Figure 4 we give representative examples of the effects produced by variations of the metal–ring plane and of the slip distances, but although configuration C always proved to be appreciably less stable than configurations A and B, we were unable to resolve clearly the question of whether the odd electron would be located in the d_{xz} or the d_{yz} orbital. Thus, as shown in Figure 4, at slip distances of less than about 1.40 Å configuration A always lay lower, but at longer values configuration B became the more stable; unfortunately the energy–distance curves exhibit very shallow minima, and within the reliability limits of our procedure these were effectively equienergetic. Nevertheless, in the region of the minima, all our calculations revealed only quite small energy separations between configurations A and B, ranging between 1500 and 3500 cm^{-1}, and averaging about 2500 cm^{-1} (0.31 eV). Finally, to test the possible effects produced by substituents on the boron atoms we carried out similar calculations for bis(1-methylborabenzene)cobalt, but again configuration C lay substantially higher (22 000 cm^{-1}) than configurations A and B, which were split only by some 1300 cm^{-1}.

It is therefore clear that for the cobalt species the molecular orbital calculations indicate unequivocably that the ground level corresponds to an essentially $^2E_1(e_2{}^4a_1{}^2e_1)$ ground state, with only a modest (ca. 2500 cm^{-1} at the most) splitting of the e_1 level, due to the heteroatoms. It is thus necessary to reexamine the available data for the cobalt bis(borabenzene) species so as to determine whether or not they can be accommodated by this conclusion. The reported magnetic moment unfortunately yields little information. Thus a value of 1.80 ± 0.1 μ_B at room temperature was found[2] for $Co(C_5H_5BOCH_3)_2$, close to the spin-only result, but this cannot be taken as an indication of a nonorbitally degenerate ground level since it has been demonstrated[9,13] that $^2E_1$ ground states may readily yield values of this order of magnitude if the effective orbital reduction factor is about 0.8, with only a small (ca. 1000 cm^{-1}) splitting of the e_1 level. Nevertheless it is worthwhile to reconsider the way in which the experimental g values for $Co(C_5H_5BC_6H_5)_2$ were assigned. Thus the spectrum in toluene–ether at 77 K yielded the g values 1.915, 1.990, and 2.130, and these were designated as g_y, g_z, and g_x, respectively (note that our labeling of the x and y axes is the opposite of that used by Herberich et al.[10]), and it was argued that the location of the odd electron in the d_{xz} or d_{yz} level would lead to $g_z < 2$, with g_x and $g_y > 2$. This was obviously inconsistent with the experimental values, but for the odd electron in the d_{z^2} level it was reasoned that one would anticipate $g_z = 2$, with $g_x > 2$ and $g_y < 2$, and this interpretation was therefore adopted.

However, this analysis effectively assumes that the separation between the d_{xz} and the d_{yz} levels is large, so it is instructive to start from the alternative basis, assuming that the ground state approximates to $^2E_1$, with only a modest splitting of the e_1 level. Here the theory is well-known and has been extensively developed by Ammeter and his collaborators[14,15] (cf. also ref 9). Thus the components of the lowest Kramers' doublet will be mixtures of dominantly d_{xz} and d_{yz} levels, the mixing coefficients, c and s, being given by the expressions $c^2 = {}^1/_2 + {}^1/_2(1 + \delta^2)^{-1/2}$ and $s^2 = {}^1/_2 - {}^1/_2(1 + \delta^2)^{-1/2}$, where $\delta = \xi_{\text{eff}}/\Delta$; here ξ_{eff} is the effective value of the 3d spin–orbit coupling constant and Δ is the splitting of the d_{xz} and d_{yz} levels produced by the deviations from pseudoaxial symmetry. With these definitions the g values are given by the relationships[9,14,15]

$$g_z = 2.0023 - 4csk_{\|}$$

$$g_{\perp} = {}^1\!/_2(g_x + g_y) = (c^2 - s^2)(2.0023 + 5x)$$

$$\Delta g = (g_y - g_x) = 6(1 + 2cs)x$$

where $k_{\|}$ is the orbital reduction factor and x is a term representing the effects of spin–orbit admixed excited states, which is approximately equal to $\xi_{\text{eff}}/\Delta E_{\text{av}}$, ΔE_{av} being the average energy above the ground state of these latter excited levels. These expressions collectively constitute the adiabatic approximation, wherein the consequences of any dynamic Jahn–Teller effects are neglected. (See however ref 14 and 15 for discussion of the inclusion of these contributions.)

In this way it is readily found that the g values measured by Herberich et al.[10] can be interpreted, assuming a distorted $^2E_1$ ground state, if one uses the assignment $g_x = 1.990$, $g_y = 2.130$, and $g_z = 1.915$, yielding the results $c = 0.9909$, $s = 0.0951$, $x = 0.0196$, $k_{\|} = 0.232$, and $\delta = 5.176$. For Co^{II} the free-ion value of ξ listed by Cole and Garrett[16] is 515 cm^{-1}; thus, assuming $\xi_{\text{eff}} = c_1{}^2\xi_{\text{free ion}}$, where c_1 (=0.6790) is our calculated metal coefficient of presence in the mainly d_{xz} or d_{yz} (singly occupied) orbital in configurations A and B, one obtains $\xi_{\text{eff}} = 237$ cm^{-1} and $\Delta = 1229$ cm^{-1}. Alternatively, if one assumes the same ξ_{eff} value as deduced by Ammeter and Swalen[14] for $CoCp_2$ (330 cm^{-1}), a splitting, Δ, of 1708 cm^{-1} results, so that a rough figure of about 1500 cm^{-1} is probably a reasonable estimate for the separation between the d_{xz} and d_{yz} levels. On the other hand, the two d–d bands reported by Herberich et. al.[10] in the electronic spectrum of bis(1-phenylborabenzene)cobalt, at 23 350 and 29 400 cm^{-1}, give $\Delta E_{\text{av}} = 26\,375$ cm^{-1}, so that from the x value $\xi_{\text{eff}} = 517$ cm^{-1} and $\Delta = 2675$ cm^{-1}. This is likely to be an overestimate, but the values of Δ deduced on the basis of the ligand field model do nevertheless show a generally good agreement in order of magnitude with the splittings obtained from the molecular orbital calculations.

Moreover, Ammeter and his collaborators have also investigated[17] the ESR behavior of bis(1-phenylborabenzene)cobalt, by both X- and Q-band measurements, as powder

Table I. Compositions of the Highest Lying Occupied Molecular Orbitals of $Fe(C_5H_5BH)_2$

							$2p_z$		$2p_{x,y}$		2s		1s	
$E(H^{core})$	$d_{x^2-y^2}$	d_{xy}	d_{z^2}	d_{xz}	d_{yz}	4s	B	C	B	C	B	C	H(B)	H(C)
−0.165	1.43		72.61	1.44		0.08	1.20	1.57	0.18	16.41	0.18	2.31	0.27	2.34
−0.181		16.50			0.40			7.95	12.40	36.53		0.77		25.40
−0.189								0.10	12.62	52.82		1.20		33.28
−0.215	40.12		15.73	0.27		0.11	6.50	4.56	1.01	19.94	0.61	4.06	2.62	4.45
−0.231							0.01	0.06	3.51	62.60	1.78	10.51	6.53	14.95
−0.248		60.16			0.49			14.66	1.15	16.11		1.37		6.06
−0.276	38.23		4.79	0.01		0.10	0.69	6.21	1.92	26.05	0.88	5.56	2.26	13.27
−0.333	0.02		0.06	15.79		0.01	14.48	44.98	0.68	12.65	0.44	0.84	0.16	9.86
−0.366		1.76			8.37			58.61	2.05	18.38		1.92		8.91

							$2p_z$		$2p_{x,y}$		2s		1s	
$E(\epsilon^{SCF})$	$d_{x^2-y^2}$	d_{xy}	d_{z^2}	d_{xz}	d_{yz}	4s	B	C	B	C	B	C	H(B)	H(C)
−0.334		37.72						8.56	9.72	28.25		0.27		15.46
−0.347	48.30		4.12	0.32			7.67	5.58	1.69	25.43	0.31	2.38	2.72	1.48
−0.360								0.26	14.07	55.44		0.30		29.90
−0.401		44.88			0.05			8.54	4.78	28.37		0.83		12.53
−0.404								0.09	7.50	64.49	0.60	5.70	10.58	11.00
−0.409	17.55		62.46	2.74		0.04	1.49	0.93	0.21	10.37	0.05	0.95	0.16	3.06
−0.425	7.21		0.08	11.36		0.08	12.73	64.03	0.25	1.73	0.03	0.15	0.29	2.07
−0.451	13.94		27.02	0.10		0.25	0.54	1.66	5.40	30.55	0.23	3.28	6.99	10.04
−0.493		1.40			8.75			82.02	0.88	3.58		0.38		2.97

samples diluted in bis(1-phenylborabenzene)iron. In both cases the results showed two *g* values significantly greater than 2 (which would appear to rule out the attribution of the odd electron to the d_{z^2} level) and one less than 2, although the actual numerical values were not too different from those reported by Herberich et al.[10] Thus the X-band powder data[17] gave *g* values of 1.9316, 2.0211, and 2.1488, assigned as g_z, g_x, and g_y, respectively, the corresponding *A* values being −49.6, −55.1, and $-139.7\ \mathrm{cm}^{-1} \times 10^{-4}$. Using the adiabatic model, one obtains $c = 0.9986$, $s = 0.0522$, $x = 0.0193$, $k_\| = 0.339$, and $\delta = 9.534$, so that the estimates for ξ_{eff} previously considered (vide supra) suggest a Δ value of about 2250–3150 cm^{-1}, while the orbital reduction factor is of a similar order of magnitude to those obtained for other distorted d^7 species. Thus, the nickelocenium cation,[15] $[NiCp_2]^+$, with $\delta = 4.74$, yields $k_\| = 0.461$, and the bis(hexamethylbenzene)iron cation,[15,18] $[Fe(HMBz)_2]^+$, gives $\delta = 5.88$ and $k_\| = 0.17$. As regards the *A* values, a first-order fitting, using the above *c* and *s* values, yields only a moderate agreement with the experimental data—$A_x = -40.8$, $A_y = -125.4$, and $A_z = -63.9$—which is not improved by the inclusion of excited-state contributions,[14] but this is not in fact altogether unexpected. Thus, although our calculations clearly show that the splitting of the e_1 (and e_2) levels in the bis(borabenzene) complexes is not very large, the departure from pseudoaxial symmetry does nevertheless have a substantial influence on the compositions of the molecular orbital levels, the most significant of which is the large degree of mixing brought about between the d_{z^2} and the $d_{x^2-y^2}$ orbitals, which clearly should be taken explicitly into account in any ligand field type calculations.

Bis(borabenzene)–Iron Systems. For the diamagnetic[3] and formally d^6 $Fe(C_5H_5BR)_2$ species the $^1A_1(e_2{}^4a_1{}^2)$ $[(d_{x^2-y^2})^2(d_{xy})^2(d_{z^2})^2]$ ground state is clearly indicated, and for this closed-shell system it is instructive to examine in more detail the orbital compositions indicated by the MO calculations. Thus in Table I we list the eigenvalues and the corresponding molecular orbital contributions for the nine highest occupied levels of $Fe(C_5H_5BH)_2$, at both the H^{core} and the ϵ^{SCF} stages of the calculation. The H^{core} situation is in addition illustrated diagrammatically in Figure 5.

It will be seen that by virtue of the boron heteroatoms the σ-type ring orbitals have been raised in energy, relative to the situation in the metallocene series, and because of the low symmetry of the bis(borabenzene) complexes, five of the highest occupied levels show extensive mixing between the metal d orbitals and the σ orbitals of the rings. Of the remaining orbitals listed two are essentially pure ligand σ orbitals with no metal d contribution, while the other two are dominantly ligand π in character with appreciable admixtures of the formally vacant metal d_{xz} and d_{yz} (e_1) levels. These latter levels in fact lie well below the metal 3d H^{core} level (at −0.202 au) and represent the main bonding interaction of the metal d orbitals; the corresponding vacant antibonding levels lie at −0.039 and −0.036 au at the H^{core} stage of the calculation and are respectively dominantly d_{xz} and d_{yz} in character with substantial ligand π contributions.

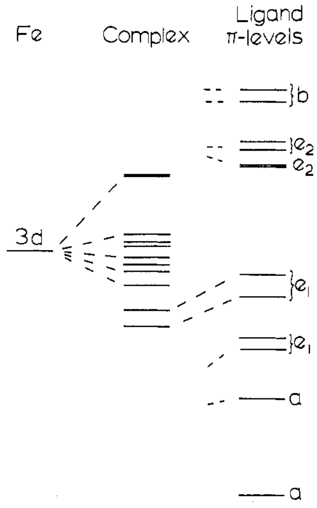

Figure 5. H^{core} diagram for 3d–ligand interaction in $Fe(C_5H_5BH)_2$.

Thus the five levels representing the metal 3d–ligand σ mixtures span a range of some 0.1 au on either side of the metal 3d H^{core} value, and the H^{core} sequence approximates to $d_{x^2-y^2} \sim d_{xy} < d_{z^2} \ll d_{xz} \sim d_{yz}$, the d_{z^2} level appearing to be very slightly antibonding and the $d_{x^2-y^2}$ and d_{xy} levels somewhat more bonding in character. The metal d-orbital contributions, taken over these five levels, amount respectively to 79.78, 76.66, 93.13, 1.72, and 0.89% for the $d_{x^2-y^2}$, d_{xy}, d_{z^2}, d_{xz}, and d_{yz} orbitals, in agreement with the formally d^6 and approximately ($e_2{}^4a_1{}^2$) configuration.

At the final ϵ^{SCF} stage of the calculation a similar situation obtains. Thus of the nine levels listed in Table I two correspond to almost pure ligand σ orbitals and two to dominantly ligand π levels with significant d_{xz} and d_{yz} admixtures, the remaining five levels again being mixtures of ligand σ orbitals and metal d orbitals. Here the corresponding metal d-orbital contributions over the five levels yield $d_{x^2-y^2}$, d_{xy}, d_{z^2}, d_{xz}, and d_{yz} values of 79.79, 82.60, 93.60, 3.16, and 0.05%, respectively, and again appreciable intra-d-orbital mixing is observed, especially between d_{z^2} and $d_{x^2-y^2}$. However, the energetic sequence of the d orbitals clearly approximates more closely now to $d_{z^2} < d_{x^2-y^2} \sim d_{xy} \ll d_{xz} \sim d_{yz}$, the vacant antibonding levels of dominantly d_{xz} or d_{yz} (plus ligand π) composition being located at +0.246 and +0.255 au, respectively. Thus the energetic ordering of the e_2 and a_1 d orbitals is reversed between the H^{core} and ϵ^{SCF} situations, and this behavior further underlines the similarities between the bis(borabenzene)iron species and the analogous metallocene system, $FeCp_2$, in which the same change of sequence has been found.[19] (See Hendrickson[19] for further discussion of the significance of this result.)

It is, of course, well-known that for sandwich species no reliance can be placed on ϵ^{SCF} sequences for the calculation of ionization potentials via Koopmans' therorem, because of the extensive reorganization effects which ensue following electron loss, and we therefore attempted to calculate the ionization energy for $Fe(C_5H_5BH)_2$ by comparison of the total energy of the neutral molecule with those of various electronic states of the corresponding cation. However, the ionization potential, when calculated in this way, does represent only a small difference between two large energy quantities, and not surprisingly the theoretical value of about 11 eV was not in very good agreement with the experimental results of around 7.7 eV for various 1-substituted derivatives.[5] Nevertheless, electron loss was correctly indicated to be more difficult than for ferrocene, although remaining easier from the metal than from the ligands, and the results did show that the $a_1(d_{z^2})$ electron was lost less readily than the $e_2(d_{x^2-y^2}$ or $d_{xy})$ electrons.

In addition we also calculated the total energies for the two components of the $^2E_2(e_2{}^3a_1{}^2)$ state of the cation (that is with the hole in either the $d_{x^2-y^2}$ or the d_{xy} orbital), and for the two components of the $^2E_1(e_2{}^4e_1)$ level (that is with the odd electron in either the d_{xz} or the d_{yz} orbital). In fact in both cases the two components of the E levels are very nearly equienergetic, the separation being less than 1000 cm^{-1}, and taking the average values yield the results $E(^2A_1) - E(^2E_2) = 1550$ cm^{-1} and $E(^2E_1) - E(^2A_1) = 29650$ cm^{-1}. From these two quantities it is, however, possible by simple ligand field arguments to obtain estimates for the effective H^{core} splitting of the 3d level. Thus one finds[9] $E(^2E_1) - E(^2A_1) = \Delta E_1 + 10B$, and $E(^2E_2) - E(^2A_1) = \Delta E_2 - 20B$, where B is the familiar Racah parameter. For the neutral $Fe(C_5H_5BCH_3)_2$ system a B value of 285 cm^{-1} may be deduced from experimental data[5] (vide infra) so that by assuming that in the cationic system this is increased in the same ratio as that by which B for $[FeCp_2]^+$ exceeds the neutral $FeCp_2$ value,[9] a figure of 350 cm^{-1} is derived, yielding the results $\Delta E_1 = 26150$ cm^{-1} and $\Delta E_2 = 5450$ cm^{-1}.

This estimate of the one-electron d-orbital splitting actually agrees very well with the values suggested by the reported electronic spectrum of bis(1-methylborabenzene)iron,[5] for which bands which may be attributed to d–d transitions were found at 27620, 32050, and 36490 cm^{-1}. If these are assigned to transitions from a $^1A_1(e_2{}^4a_1{}^2)$ ground state to $^1E_1$, $^1E_2$, and $^1E_1$ levels, respectively, assuming approximate pseudoaxial symmetry, the parameters $\Delta E_1 = 27200$ cm^{-1}, $\Delta E_2 = 8550$ cm^{-1}, and $B = 285$ cm^{-1} are readily obtained,[9,20,21] lending further support to the contention that the departure from effectively axial symmetry is small.

Thus in the borabenzene series ΔE_2 proves to be of about the same order of magnitude as for ferrocene (7100 cm^{-1}),[9] but ΔE_1 substantially exceeds the $FeCp_2$ value (22000 cm^{-1}).[9] As expected therefore the B value for the bis(borabenzene)iron compound (285 cm^{-1}) is appreciably smaller than that found for $FeCp_2$ (390 cm^{-1}), the corresponding nephelauxetic ratios being 0.31 and 0.42, respectively. Moreover, because of the larger ΔE_1 and ΔE_2 values in the borabenzene series it is to be expected that the d–d bands in the electronic spectrum of bis(1-phenylborabenzene)cobalt, reported by Herberich et al.,[10] should lie at higher energies than the similar bands for cobaltocene, as is in fact observed, and the d–d bands of the borabenzene system should, of course, be assigned in the same way as for cobaltocene.[9]

Finally, calculations were also carried out on the substituted derivative bis(1-methylborabenzene)iron, $Fe(C_5H_5BCH_3)_2$, which is known experimentally. However, although minor differences between these results and those for the parent system were evident, the eigenvectors, bond orders, and charge distributions, etc. were so similar that it was clear that no significant changes were thereby brought about, thus reinforcing the conclusions drawn from the results for the Co systems.

Bis(borabenzene)–Manganese Systems. Although the symmetrical bis(borabenzene) derivatives of manganese are not yet known, (1-phenylborabenzene)manganese tricarbonyl, $(C_5H_5BC_6H_5)Mn(CO)_3$, has been prepared by Herberich and Becker,[22] and it therefore appeared worthwhile to carry out a few calculations for the bis(borabenzene) species. Since these results were restricted to just a single value of both the slip distance and the metal–ring distance (1.31 and 1.60 Å, respectively), their predictive value is obviously limited, but at the distances shown our results indicate the $^2E_2(e_2{}^3a_1{}^2)$ and $^2A_1(e_2{}^4a_1)$ levels to be almost exactly equal in energy, with the $^6A_1(e_2{}^2a_1e_1{}^2)$ state 1.28 eV (10325 cm^{-1}) higher. Thus the Mn system would be intermediate in behavior between the bis(benzene) series, for which $^2A_1$ always lies lowest, and the metallocenes, which show either a $^6A_1$ ground level, as in $MnCp_2$, or a $^2E_2$ ground state, as in $[FeCp_2]^+$. Clearly, variations in the relative energies of the $Mn(C_5H_5BH)_2$ states would be expected with changes in the distance parameters, but such further calculations were not felt to be justified in the absence of experimental data.

Bis(borabenzene)–Chromium Systems. The two bis(borabenzene)chromium complexes so far synthesized were found to be paramagnetic, with room-temperature magnetic moments of 3.3 ± 0.1 and 3.0 ± 0.1 μ_B for the 1-methyl and 1-phenyl derivatives, respectively.[6] These results are indeed significant since the values obtained are clearly above the spin-only result (2.83 μ_B), thus suggesting an orbital contribution to the moment: in fact the results are very similar to that obtained[23,24] for the analogous metallocene chromocene, $CrCp_2$, for which a value of 3.10 μ_B was found between 83 and 298 K. In the latter case it was shown[13,24] that the experimental data could be accommodated with an orbital reduction factor, $k_{\parallel}$, of ca. 0.7–0.8, and a modest, ca. 500–600 cm^{-1}, orthorhombic splitting of the $e_2(d_{x^2-y^2},d_{xy})$ level, and it is therefore reasonable to assume that a similar situation obtains for the bis(borabenzene)chromium species. Moreover, the smaller moment observed for the phenyl derivative accords with the expectation of a larger splitting for this substituent than for the methyl group.

Furthermore, our MO calculations also support the conclusion that the ground state is an essentially $^3E_2(e_2{}^3a_1)$ level rather than the alternative $^3A_2(e_2{}^2a_1{}^2)$ state, and the former is found to lie some 0.60 eV (ca. 4850 cm^{-1}) lower. In addition, the splitting between the two components of the $^3E_2$ level, with the hole in the $d_{x^2-y^2}$ or the d_{xy} level, is only about 0.14 eV (ca. 1000 cm^{-1}), the former lying lower, which is also in good agreement with the ligand field reasoning and with our

Table II. Electronic Populations for the Free $(C_5H_5BH)_2$ System and the Complex $Fe(C_5H_5BH)_2$

orbitals	free $(C_5H_5BH)_2$	$Fe(C_5H_5BH)_2$
C_2, $2p_z$ (π)	1.079	0.996
C_3, $2p_z$ (π)	0.994	0.952
C_4, $2p_z$ (π)	1.127	1.019
B_1, $2p_z$ (π)	0.728	0.677
C_2, 2s, $2p_{x,y}$ (σ)	2.926	2.884
C_3, 2s, $2p_{x,y}$ (σ)	3.238	3.148
C_4, 2s, $2p_{x,y}$ (σ)	2.798	2.742
B_1, 2s, $2p_{x,y}$ (σ)	2.522	2.432
H_2, 1s	1.163	1.084
H_3, 1s	0.852	0.804
H_4, 1s	1.119	1.042
H_1, 1s	1.199	1.115
Fe, $3d_{z^2}$		1.962
Fe, $3d_{xz}$		0.447
Fe, $3d_{yz}$		0.352
Fe, $3d_{x^2-y^2}$		1.766
Fe, $3d_{xy}$		1.732
Fe, 4s		0.515
Fe, 4p		1.684

Table III. Changes in Electronic Populations of Sandwich Ligands on Complexation

molecule[a]	gain (+) or loss (−) of population on complexation
$FeCp_2$	Cp(σ), −0.255; Cp(π), −0.630; Cp(H), −0.440
$CrBz_2$[b]	Bz(σ), −0.618; Bz(π), +0.323; Bz(H), +0.055
CpMnBz[c]	Cp(σ), −0.135; Cp(π), −0.630; Cp(H), −0.390
	Bz(σ), −0.648; Bz(π), +0.712; Bz(H), −0.048
CpCrCh[d]	Cp(σ), −0.095; Cp(π), −0.650; Cp(H), −0.385
	Ch(σ), −1.204; Ch(π), +1.650; Ch(H), +0.413
CpNiCpr[e]	Cp(σ), −0.280; Cp(π), −0.825; Cp(H), −0.390
	Cpr(σ), −0.840; Cpr(π), +1.236; Cpr(H), +0.261
CpCoCb[f]	Cp(σ), −0.20; Cp(π), −0.85; Cp(H), −0.50
	Cb(σ), −0.08; Cb(π), −1.40; Ch(H), −0.72
$Fe(C_5H_5BH)_2$	C_5H_5BH(σ), −0.410; C_5H_5BH(π), −0.409; C_5H_5BH(H), −0.415

[a] Cpr = π-C_3H_3, Cb = π-C_4H_4, Cp = π-C_5H_5, Bz = π-C_6H_6, Ch = π-C_7H_7. [b] D. W. Clack and W. Smith, *Inorg. Chim. Acta,* **20,** 93 (1976). [c] D. W. Clack and K. D. Warren, *J. Organomet. Chem.,* **157,** 421 (1978). [d] D. W. Clack and K. D. Warren, *Theor. Chim. Acta,* **46,** 313 (1977). [e] D. W. Clack and K. D. Warren, *J. Organomet. Chem.,* **149,** 401 (1978). [f] D. W. Clack and K. D. Warren, *Inorg. Chim. Acta,* **27,** 105 (1978).

previous findings of small splittings of the e levels.

Bonding Characteristics of the Borabenzene Ligand. In attempting to compare the bonding properties of the borabenzene ligand with those of similar entities, such as Cp and Bz, it is convenient to consider in further detail the results for the iron system $Fe(C_5H_5BH)_2$, since this formally approximated to a closed-shell $d^6(e_2{}^4a_1{}^2)$ system which may readily be compared both with the analogous $FeCp_2$ and also with the d^6 complex containing the corresponding homocyclic (Bz) ring, $CrBz_2$. Initially therefore we examine the charge distributions which result from our calculations, both for the iron complex and for the system of two borabenzene rings (at the same separation distance) lacking the iron atom.

Thus in Table II are shown these results for the two systems, together with a breakdown of the changes in electronic populations produced by complex formation for the σ and π frameworks and the hydrogen atoms of the ligand. For comparison we also list similar summarized results for other sandwich and mixed-sandwich species (Table III).

It is evident that for $Fe(C_5H_5BH)_2$ electron density is lost from all the ligand orbitals on complexation to the metal, and the borabenzene ligand thus resembles the Cp ligand more than any other ring system. However, although electron donation from the borabenzene e_1 π levels into the formally vacant iron $e_1(d_{xz},d_{yz})$ levels is, as for the metallocenes, the primary bonding mechanism, the extent of ligand→metal electron accession from the π framework is not so great as for Cp systems, and the σ contribution is of roughly equal magnitude. Nevertheless, the borabenzene ligand is seen to behave in marked contrast to the unsubstituted Bz ring system, for which a substantial metal→ligand π back-donation from the $e_2(d_{x^2-y^2}, d_{xy})$ levels is found, thus suggesting that the e_2 interaction is appreciably less important than in MBz_2 species.

Table IV. Comparison of Metal 3d–Ligand Bond Orders Per Ring for $Fe(C_5H_5BH)_2$, $FeCp_2$, and $CrBz_2$

metal 3d levels	bond orders		
	2s	$2p_x + 2p_y$	$2p_z$
	$Fe(C_5H_5BH)_2$		
a_1 d_{z^2}	0.031	0.091	0.072
e_1 $d_{xz} + d_{yz}$	0.339	0.725	0.916
e_2 $d_{x^2-y^2} + d_{xy}$	0.138	0.159	0.905
	$FeCp_2$		
a_1 d_{z^2}	0.015	0.127	0.042
e_1 $d_{xz} + d_{yz}$	0.297	0.506	0.958
e_2 $d_{x^2-y^2} + d_{xy}$	0.134	0.066	0.696
	$CrBz_2$		
a_1 d_{z^2}	0.010	0.167	0.053
e_1 $d_{xz} + d_{yz}$	0.282	0.463	0.684
e_2 $d_{x^2-y^2} + d_{xy}$	0.119	0.045	1.380

In short the $Fe(C_5H_5BH)_2$ results indicate that the bonding in the bis(borabenzene) complexes exhibits three salient features: (1) Due to the low overall symmetry a substantial measure of intra-d-orbital mixing is brought about, especially between the d_{z^2} and $d_{x^2-y^2}$ orbitals and to a lesser extent between the d_{xy} and d_{yz} levels. Nevertheless, one finds that the overall situation in the d^6 system actually does correspond closely to the formal double occupation of the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} levels and that on ionization an electron is essentially fully removed from one or other of these orbitals, despite the mixing indicated by the eigenvectors. (2) Due to the more electropositive character of the boron atom the σ levels of the rings are moved to higher energies relative to the Cp and Bz systems. Consequently, more ligand σ-orbital participation in the bonding is to be expected and is clearly evidenced for the interaction of the metal d_{z^2}, $d_{x^2-y^2}$, and d_{xy} levels. (3) The dominant bonding interaction remains the same as in the metallocene series and results from the interaction of the filled ligands π e_1 orbitals with the vacant metal d_{xz} and d_{yz} levels. This leads to strongly bonding, dominantly ligand e_1 π levels, with substantial metal d_{xz} and d_{yz} contributions. In confirmation of this the $Co(C_5H_5BH)_2$ system (configurations A and B) exhibits a highest singly occupied e_1 level in which the metal d_{xz} or d_{yz} contribution is only 46.1% with very substantial ligand π admixtures (42.1%).

Finally, it is enlightening to compare the calculated bond orders per ring for the metal d orbitals and the ligand σ (2s, $2p_{x,y}$) and π ($2p_z$) orbitals with those calculated[1] for the related $FeCp_2$ and $CrBz_2$ species. For the iron complex, $Fe(C_5H_5BH)_2$, the bond orders per ring found for the d_{xz}, d_{yz} and $d_{x^2-y^2}$, d_{xy} components of the e_1 and e_2 levels, respectively, do differ somewhat as would be expected in the lower symmetry, but we have listed the total values as shown in Table IV so as to facilitate comparison with the other data. It will be seen that the metal–ligand σ bond orders for the bis(borabenzene) complex are generally significantly greater than for the other two systems, as already expected and concluded, whereas the e_2 metal–ligand π bonding is greater than for $FeCp_2$ but less than for $CrBz_2$, as previously predicted (vide supra). Similarly, the e_1 metal–ligand π bonding is very slightly less than in $FeCp_2$ but appreciably greater than in $CrBz_2$ which also accords with our previous expectations. To sum up therefore, the borabenzene ligand shows bonding behavior intermediate between those of the Cp and Bz ligands, although more closely akin to the former, and behaves in a manner consistent with the predictions of the ligand field approach.

Registry No. $Cr(C_5H_5BH)_2$, 68344-21-8; $Mn(C_5H_5BH)_2$, 68344-22-9; $Fe(C_5H_5BH)_2$, 68344-23-0; $Co(C_5H_5BH)_2$, 68378-62-1; $Fe(C_5H_5BCH_3)_2$, 54853-80-4; $Co(C_5H_5BCH_3)_2$, 36534-27-7.

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Notes

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Structure of Pentakis(urea)dioxouranium(VI) Nitrate, $[UO_2(OC(NH_2)_2)_5](NO_3)_2$[1]

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In our ongoing studies of uranium complexes we have determined the crystal structure of $UO_2(OC(NH_2)_2)_5(NO_3)_2$ by X-ray diffraction. Gentile and Campisi[2] reported the preparation of this compound and concluded, on the basis of infrared spectra, that the nitrate groups are not coordinated to uranium, a fact which we confirm. The uranyl ion is coordinated by oxygen atoms of the five urea molecules in a complex which is monomeric, not a polymer as suggested earlier.[2]

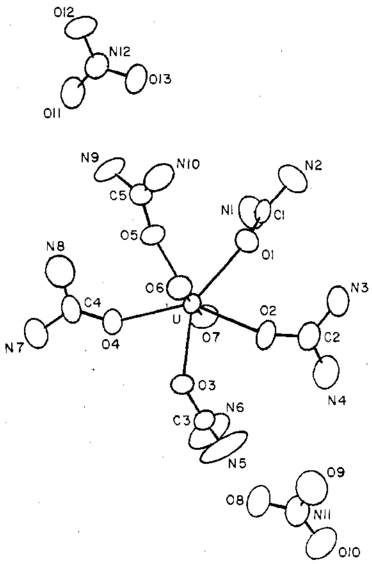

Figure 1. ORTEP view of $[UO_2(OC(NH_2)_2)_5][NO_3]_2$ showing the numbering scheme.

Experimental Section

From an aqueous solution of uranyl nitrate and urea which was allowed to evaporate slowly overnight, small fluorescent lime green crystals precipitated. The crystals were stable in air and showed no decomposition during the 2 weeks the X-ray experiments were being conducted. Weissenberg photography showed the crystal to be monoclinic, and rough cell dimensions were obtained.

A crystal of dimensions 0.08 × 0.11 × 0.21 mm was glued to a glass fiber and examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.709 30 Å). ω scans of the 800, 040, and 006 reflections showed peaks with half-widths of 0.16, 0.15, and 0.11°, respectively. The setting angles of eight manually centered reflections ($16° < 2\theta < 25°$) using Mo $K\beta$ (λ 0.632 288 Å) and three reflections ($40° < 2\theta < 43°$) using Mo $K\alpha_1$ were used to determine the cell parameters $a = 15.944$ (8) Å, $b = 8.952$ (4) Å, $c = 15.394$ (6) Å, $\beta = 106.31$ (3)°, and $V = 2108.8$ Å^3. The observed extinctions are unique to space group $P2_1/n$. For $Z = 4$ and a molecular weight of 694.32 the calculated density is 2.19 g cm^{-3}.

Intensity data were collected with a scan speed of 2°/min on 2θ. Each reflection was scanned from 0.7° before the $K\alpha_1$ peak to 0.7° after the $K\alpha_2$ peak, and backgrounds were counted for 4 s at each end of the scan range. The temperature during data collection was 21 ± 1 °C. Three standard reflections were measured after every 200th scan. The 10 524 scans, not including standards, resulted in 4869 unique intensities, 2954 of which were greater than 3σ. An absorption correction was applied,[3] $\mu = 73$ cm^{-1}, and the maximum and minimum corrections were 2.24 and 1.77, respectively. The intensities of all three standards decayed about 3% during the data collection period, and the data were corrected accordingly.

The trial coordinates of the uranium atom position were derived from a three-dimensional Patterson function. The Fourier map, calculated with the phases of the uranium atom alone, revealed 11 of the light atoms. A least-squares refinement and the subsequent Fourier calculation, phased by the 12 atoms, revealed the locations of the remaining atoms. A series of least-squares refinements in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized coverged rapidly to the final structure. The expressions that were used in processing the data and estimating the weights are available as supplementary material; the "ignorance factor", p, was set to 0.03. Scattering factors from Doyle and Turner[4] were used, and anomalous dispersion corrections[5] (for U, $f' = -10.673$ and $f'' = 9.654$) were applied. Hydrogen atoms could not be identified in the final difference maps and were not included in the least-squares refinement. The largest peak in the last difference Fourier map was 1.2 e. Anisotropic thermal

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