a unit sphere. A plot of a semiquantitative measure of the correlation between model and observation over the surface of a sphere each for models A and B enabled location of all trial sets of exchange parameters.

Registry No. $[FeS_4C_4(CF_3)_4]_2$, 41959-83-5.

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Optical and Magnetic Properties and Geometry of Some d^5 Ruthenium Complexes

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Magnetic and optical properties of two d^5 ruthenium–triphenylarsine complexes have been investigated. The complexes have D_{4h}, C_{2v}, and D_{3h} molecular symmetries. The complex $RuCl_3[As(C_6H_5)_3]_2$ has been found to possess C_{2v} symmetry in the solid state and a trigonal-bipyramidal geometry (D_{3h}) in solution. The D_{3h} geometry has been established on the basis of the dipole moment measurement, optical spectra, and epr results. Optical spectra of all complexes have been correlated with the epr g values. One of the L → L charge-transfer transitions involving the $\pi \rightarrow \pi^*$ transitions in the phenyl rings shows fine structures, better resolved than what has been reported for triphenylarsine ligand, and is considerably blue shifted in the trigonal-bipyramidal molecule, indicating a large amount of conjugation between arsenic and benzene through d_π–p_π interactions.

Introduction

Several low-spin d^5 complexes of second- and third-row transition metal ions with arsines and phosphines as ligands have been reported in the literature.[2-7] Ruthenium(III) and osmium(III) form quite a large number of these complexes and seem to possess a wide variation in geometry. Magnetic susceptibility and esr measurements have been used to identify their symmetries and establish the low-spin nature of these compounds. So far, no attempt has been made to interpret the optical spectra in detail, nor have the solution properties been studied. In this report, we have tried to interpret the optical and magnetic properties of two complexes: $RuCl_3(CH_3OH)(AsPh_3)_2$ (I) with a C_{2v} symmetry and $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$ (II) with a D_{4h} symmetry in both solid and solution states. We report the conversion of I into a trigonal-bipyramidal molecule in benzene with interesting magnetic and electronic structures.

Experimental Section

Reagents. Ruthenium trichloride hexahydrate and triphenylarsine were obtained from Alfa Inorganics. Organic solvents are spectral grade. The complexes I and II were prepared according to the methods of Stephenson and Wilkinson[5b] and Stephenson, respectively,[5a] and were recrystallized in proper solvents.

Preparation of $RuCl_3(AsPh_3)_2$. The green compound, I, was ground in a mortar; the color changed to brown. This was extracted into benzene and filtered from any insoluble residue. The filtrate was evaporated at room temperature to dryness. This was redissolved in benzene; deep brown crystals of $RuCl_3(AsPh_3)_2$ (III) were obtained by slow crystallization from the solution. *Anal.* Calcd: C, 52.7; H, 3.69. Found: C, 52.9; H, 3.8.

Physical Measurements. The dipole moment of III in benzene at various concentrations was measured by a microwave method.[8] The electronic spectra were measured in methanol, benzene, and isooctane, using Cary Model-14 and Carl Zeiss DMR-21 instruments.

The electron paramagnetic resonance (epr) spectra were measured in a Varian E-4 epr instrument with 100-kHz modulation. The spectral g values were calibrated with DPPH standard.

Results

Electron Paramagnetic Resonance. The epr spectra of the polycrystalline samples of green $RuCl_3(CH_3OH)(AsPh_3)_2$ (I) and brown $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$ (II) were measured at both room and liquid nitrogen temperatures. Both of them exhibit almost similar spectra, characteristic of an axially symmetric complex with a $g_\parallel$ around 1.71 and $g_\perp$ around 2.46–2.52. The isotropic g value turns out to be 2.20–2.23. Compound II does not exhibit any change in g value pattern when brought into benzene solution. Also, compound I in benzene or methanol solutions exhibits the same g values as in the solid state. However, when I is ground in a mortar, dissolved in benzene, and evaporated to a brown solid, then the epr measurement of this brown solid, identified by analysis as $RuCl_3(AsPh_3)_2$ (III), shows only a small change in the g values. The g values of III were measured to be $g_\parallel = 1.73$ and $g_\perp = 2.41$, with a $g_{av} = 2.18$, not too different from those values obtained for I and II. However, when the epr of III in benzene solution was measured, it showed drastic changes. At room temperature, the g_{av} was measured to be 2.30 as opposed to that calculated for compounds I-III (solid) to be in region 2.18–2.23. The same, when cooled to liquid nitrogen temperature, showed a spectrum characteristic of axial symmetry with $g_\parallel = 2.00$ and $g_\perp = 2.48$ resulting in a calculated $g_{av} = 2.32$. Though the value for $g_\perp$ did not show any remarkable change from those of I-III, there was a drastic shift in $g_\parallel$ to that of a free-electron value. This is indicative of a gross change in geometry in solution. All the epr results are given in Table I. The epr spectra of all these compounds at liquid nitrogen temperature are shown in Figure 1 for the sake of comparison. None of the spectra revealed any hyperfine interaction due to the nuclei with magnetic moments, *viz.*, Ru, As, and Cl.

Dipole Moment. The dipole moment of the benzene solution of compound III was measured to be nearly zero at various concentrations.

Electronic Spectra. Compounds I and II showed similar spectra with bands at 24,510 (ϵ 1065) and 28,820 cm^{-1} (ϵ

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Table I. Epr Parameters of Ruthenium Complexes

No.	Compd	State	Temp, °K	$g_\parallel$	$g_\perp$	$\langle g \rangle$
I	$RuCl_3(CH_3OH)(AsPh_3)_2$	Solid	300	1.67	2.46	2.20
		Solid	77	1.71	2.52	2.25
		Frozen glass in benzene	77	1.72	2.46	2.21
II	$N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$	Solid	300	1.71	2.50	2.23
		Solid	77	1.73	2.49	2.24
III	$RuCl_3(AsPh_3)_2$	Solid	300	1.73	2.41	2.18
		Solid	77	1.73	2.41	2.18
IV	$RuCl_3(AsPh_3)_2$	Benzene soln	77	2.00	2.48	2.32

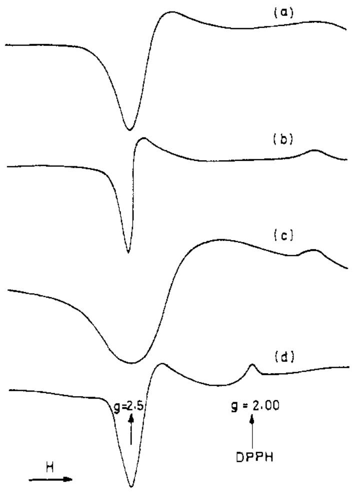

Figure 1. Epr spectra of (a) solid $RuCl_3(CH_3OH)(AsPh_3)_2$ at liquid nitrogen temperature, (b) solid $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$ at liquid nitrogen temperature, (c) solid $RuCl_3(AsPh_3)_2$ at room temperature, and (d) frozen glass of $RuCl_3(AsPh_3)_2$ in benzene at liquid nitrogen temperature.

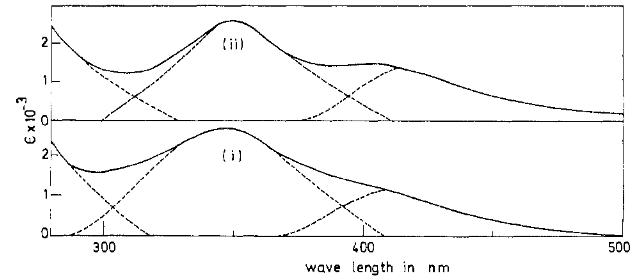

Figure 2. Electronic spectra in the 1000-320-nm region of (i) $RuCl_3(CH_3OH)(AsPh_3)_2$ in methanol and (ii) $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$ in methanol.

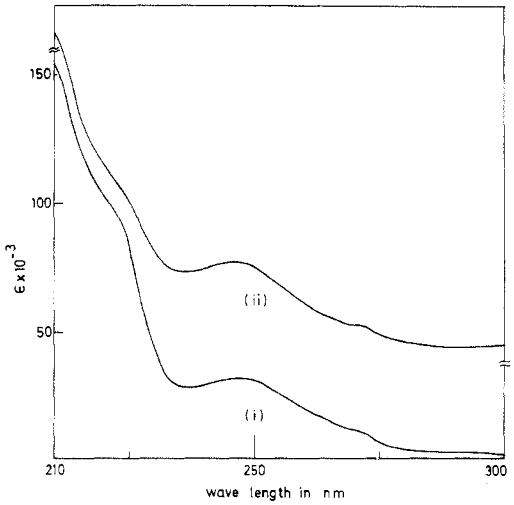

Figure 3. Electronic spectra in the 300-210-nm region of (i) $RuCl_3(CH_3OH)(AsPh_3)_2$ in methanol and (ii) $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$ in methanol.

2500). In the ultraviolet region, a strong band was obtained with a shoulder containing a series of peaks in the region 270-255 nm, *i.e.*, 37,170-39,600 cm^{-1}, very well separated. At the top of this band was found a peak at 40,320 cm^{-1}. Yet another absorption occurred at 221 nm, *i.e.*, 45,250 cm^{-1}. The spectra are shown in Figures 2 and 3. The spectral results appear in Table II. We could not obtain a good spectrum of solid III in Nujol mull though the visible region spectrum seems to have a pattern similar to that of complexes I and II.

The electronic spectra of III in isooctane solution are given in Figures 4 and 5. Instead of only two bands in the visible region observed for the complexes I and II, compound III in isooctane solution exhibits four bands, one in the ir region and three in the visible region, namely, at 12,880 (ϵ 590), 18,350 (ϵ 2900), 24,390 (ϵ 6200), and 27,770 cm^{-1} (ϵ 2400). Another most interesting observation was in the uv region pertaining to the intraligand charge transfers. While the structureless transition involving the lone pair has red shifted considerably to 36,240 cm^{-1} (ϵ 19,000), the band with structures is blue shifted to 40,320 cm^{-1} ($\epsilon \sim 10{,}000$) and forms part of the high-energy shoulder of the band. Another absorption maximum occurs at 45,250 cm^{-1} (ϵ 31,000). The results are given in Table III and the spectra in Figures 4 and 5. For comparison purposes, the uv spectrum of the triphenylarsine ligand is included in Figure 5.

Ligand Field Model. Some authors have worked on the one-electron orbital schemes for the trigonal-bipyramidal d^6, d^7, and d^8 complexes[9-11] and their results have been successfully used by other authors for interpreting their spectral results.[12,13] Here we have calculated the excited-state energies in terms of crystal field parameters *Ds* and *Dt* and Slater-Condon electron repulsion parameters F_0, F_2, and F_4 for explaining the possible crystal field bands which may appear in a strong-field, low-spin d^5 ruthenium(III) trigonal-bipyramidal complex. With the axial and equatorial charges of Z_A and Z_E at distances of *a* and *b*, respectively, from the central metal atom, the *Ds* and *Dt* are defined as

$$Ds = \frac{1}{14}\left[\frac{4Z_A}{b^3} - \frac{3Z_E}{a^3}\right]\langle r^2 \rangle$$

$$Dt = \frac{1}{168}\left[\frac{16Z_A}{b^5} + \frac{9Z_E}{a^5}\right]\langle r^4 \rangle$$

Also, under the D_{3h} point group, the d orbitals transform as $e'(x^2-y^2, xy)$, $e''(xz, yz)$, and $a_1'(z^2)$. Their one-electron energies have been calculated as $-2Ds + Dt$, $Ds - 4Dt$, and $2Ds + 6Dt$, respectively. Assuming very strong in-plane σ and π overlaps and a fairly weak axial overlap, we have taken into consideration the one-electron d ordering as $e'' < a_1' < e'$. The low-energy crystal field energies have been calculated for states arising from the electronic configurations $(e'')^4(a_1')^1$ (leading to a ground state $^2A_1'$) and $(e'')^3(a_1')^2$, $(e'')^4(e')^1$, and $(e'')^3(a_1')^1(e')^1$ which are all listed in Table IV. However, only a few relevant states and their energies for the last configuration are given in this paper.[14] The ex-

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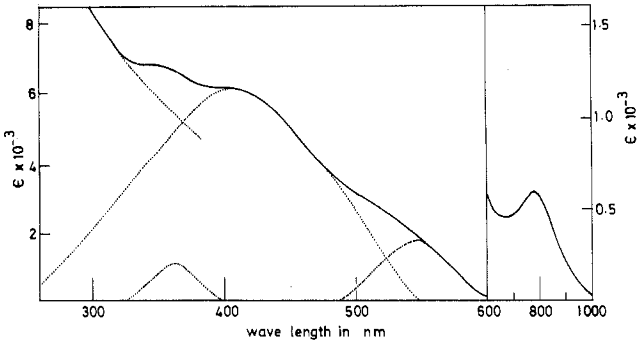

Figure 4. Electronic spectrum of $RuCl_3(AsPh_3)_2$ in benzene in the 1000–320-nm region.

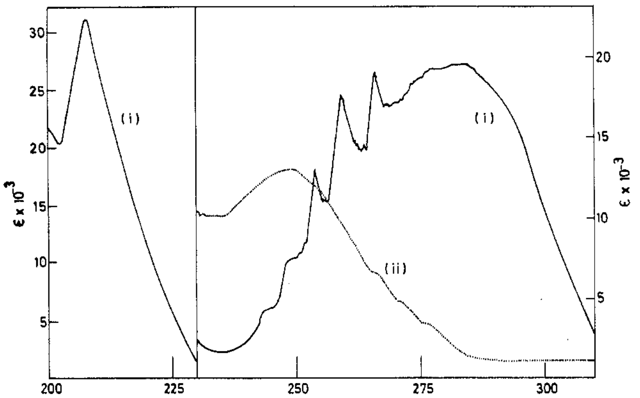

Figure 5. Electronic spectra (320–210 nm region) of $RuCl_3(AsPh_3)_2$ in isooctane (full lines) and the triphenylarsine ligand in isooctane (dotted lines).

Table II. Absorption Spectral Results of $RuCl_3(CH_3OH)(AsPh_3)_2$ and $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$ in Methanol and Their Assignments

Absorption maxima			
nm	cm^{-1}	ϵ, M^{-1} cm^{-1}	Assignment
408	24,510	1065	$^2B_{2g} \rightarrow {}^2B_{1g}$
347	28,820	2500	$^2B_{2g} \rightarrow {}^2E_g(2)$
269	37,170	~10,000	$\pi \rightarrow \pi^*$
263	38,020		
257	38,910		
255	39,210		
248	40,320	33,300	Charge transfer involving As lone pair and benzene ring
221	45,250	60,700	M → L or L → M

Table III. Electronic Spectrum of $RuCl_3(AsPh_3)_2$ in Solution (TBP)

Absorption maxima			
nm	cm^{-1}	ϵ, M^{-1} cm^{-1}	Assignment
776	12,880	590	$^2A_1' \rightarrow {}^2E''$
545	18,350	2,900	$^2A_1' \rightarrow {}^2E'$
410	24,390	6,200	$^2A_1' \rightarrow {}^2A_2''(I)$
360	27,770	2,400	$^2A_1' \rightarrow {}^2A_2''(II)$
276	36,230	19,000	Charge transfer involving As lone pair and benzene ring
268	37,310	~10,000	$\pi \rightarrow \pi^*$
261	38,320		
254	39,370		
248	40,320		
243	41,150		
238	42,020		
208	48,080	31,000	Not clear

citation energies in the strong ligand field model and the proposed assignments are also listed in Table IV. An attempt will now be made to interpret the electronic spectral results in the light of epr data.

Discussion

Compounds I and II are paramagnetic[5,6] ($S = 1/2$) and have almost identical optical spectral and magnetic properties. Also the optical spectrum of another similar d^5 ruthenium complex with the formula *mer*-$RuCl_3(As(n\text{-}Pr)_3)_3$ exhibits electronic bands[7] at 15,600, 20,000, 23,500, 33,800, and and 37,700 cm^{-1} while I and II have entirely different electronic spectra with only two bands at 24,510 and 28,820 cm^{-1} in addition to the intraligand charge-transfer bands occurring at higher energies. So, I and II can have a symmetry quite different from that of *mer*-$RuCl_3(As(n\text{-}Pr)_3)_3$ and we may safely assume (as to be proved below) that they have C_{2v} and D_{4h} point groups, respectively. Also, because of their similar spectral and magnetic properties, discussion on any one of them will apply equally well to the other. Because a higher symmetry would facilitate discussion, we shall begin with II which has a D_{4h} symmetry with a low-spin d^5 configuration.

Assuming a one-electron odering of $e_g(xz, yz) < b_{2g}(xy) < a_{1g}(z^2) < b_{1g}(x^2 - y^2)$, the ground-state electronic configuration is $(e_g)^4(b_{2g})^1$, leading to a $^2B_{2g}$ ground state. The energy levels of a tetragonally distorted d^5 complex are given in Figure 6. We can calculate the energies of the ground and excited states in terms of Dq and distortion parameters[15] Ds and Dt and Slater–Condon energies in a manner similar to that of Gray and Ballhausen[16] for a d^5 complex. The first two electronic bands at 24,510 and 28,820 cm^{-1} are being assigned of crystal field origin. On the basis of the calculation for a D_{4h} d^5 complex, the energy separation[16] between $^2B_{2g}$ and $^2B_{1g}$ would amount to only $10Dq$. The first band at 24,510 cm^{-1} is assigned to this transition $^2B_{2g} \rightarrow {}^2B_{1g}$ ($xy \rightarrow x^2 - y^2$ in one-electron terminology) because the Dq value of 2450 cm^{-1} for this complex is in excellent agreement with a Dq value of 2400 cm^{-1} calculated[17-19] for $RuCl_6^{3-}$, taking into consideration that there will be little difference[20] in the ligand field strength of Cl^- and $AsPh_3$. The second band at 28,820 cm^{-1} is assigned to $^2B_{2g} \rightarrow {}^2E_g(2)$. Any transition from $^2B_{2g} \rightarrow {}^2E_g(1)$ will be very low in energy as is to be shown below.

With the assumption of $^2B_{2g}$ ground state and the first band assignment to $^2B_{2g} \rightarrow {}^2B_{1g}$, we can calculate the $g_\parallel$ value and compare it with the experimental one. The simple expression for $g_\parallel$ is

$$g_\parallel = 2.0023\left(1 - \frac{4\lambda}{\Delta_\parallel}\right)$$

Using $\lambda = 1000$ cm^{-1} for the Ru^{3+} ion in complexes[21,22] and $\Delta_\parallel(^2B_{2g} \rightarrow {}^2B_{1g})$ as 24,510 cm^{-1}, the calculated $g_\parallel$ value

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Table IV. Calculated Results on Low-Energy Crystal Field Bands for a Low-Spin d^5 Trigonal-Bipyramidal Complex[a]

Confign	States[b]	Energy expression	Electronic transition[c]	Excitation energy[d]	Assigned band, cm^{-1}
$(e'')^4(a_1')^1$	$^2A_1'$	$6Ds - 10Dt + 10F_0 - 140F_4$			
$(e'')^3(a_1')^2$	$^2E''$	$7Ds + 10F_0 + 10F_2 - 190F_4$	$^2A_1' \rightarrow {}^2E''$ (forbidden)	$Ds + 10Dt + 10F_2 - 50F_4$	12,880
$(e'')^4(e')^1$	$^2E'$	$2Ds - 15Dt + 10F_0 - 20F_2 - 40F_4$	$^2A_1' \rightarrow {}^2E'$ (x,y allowed)	$-4Ds - 5Dt - 20F_2 + 100F_4$	18,350
$(e'')^3(a_1')^1(e')^1$	$^2A_2''$(I)	$3Ds - 5Dt + 10F_0 - \frac{42}{4}F_2 - \frac{490}{4}F_4$	$^2A_1' \rightarrow {}^2A_2''$(I) ($z$ allowed)	$-3Ds + 5Dt - 13.6F_2 + 33.2F_4$	24,390
	$^2A_2''$(II)	$3Ds - 5Dt + 10F_0 - \frac{138}{12}F_2 - \frac{1410}{12}F_4$	$^2A_1' \rightarrow {}^2A_2''$(II) ($z$ allowed)	$-3Ds + 5Dt - 8.3F_2 + 6.8F_4$	27,770

[a] Values for parameters in cm^{-1}: $Ds = -9820$; $Dt = +1631$; $F_2 = 1283$; $F_4 = 129$. Ratio $F_2/F_4 = 9.96$. [b] For the configuration $(e'')^3(a_1')^1(e')^1$, only the states leading to allowed transitions are mentioned here. The rest of the states, though calculated, are not mentioned in this paper. [c] The transition $^2A_1' \rightarrow {}^2E''$ may be made allowed by coupling with E'', E', or A_2'' modes of vibration. [d] Excitation energy for the last two transitions listed in the table were calculated assuming configuration interaction. The off-diagonal matrix element between $^2A_2''$(I) and $^2A_2''$(II) is $(3\sqrt{3}/2)[-F_2 + 5F_4]$.

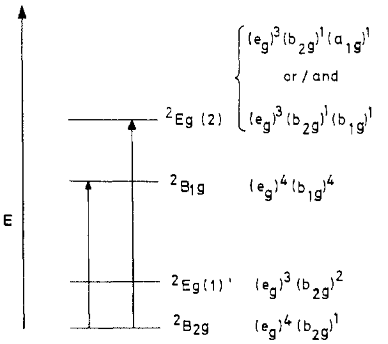

Figure 6. Energy levels of $[RuCl_4(AsPh_3)_2]^-$.

of 1.74 is in excellent agreement with the experimental value of 1.73 measured at liquid nitrogen temperature, supporting the correctness of the ground state and the assignment of the first band as lowest energy crystal field band. Though a similar attempt could be made at calculating $g_\perp$, the transition $^2B_{2g} \rightarrow {}^2E_g(1)$ was not observed, probably because of its very low transition energy. However, one could prove the very low-energy nature of this transition from the measured $g_\perp$ value and the above-mentioned λ value. By using the simple expression for $g_\perp$, namely, $g_\perp = 2.0023(1 - \lambda/\Delta_\perp)$ and experimental $g_\perp = 2.49$ and $\lambda = -1000$ cm^{-1}, we immediately calculate a value of 4000 cm^{-1} for $\Delta_\perp$, *i.e.*, $^2B_{2g} \rightarrow {}^2E_g(1)$. This indicates a fairly low distortion of the complex from a regular octahedron.

The charge-transfer spectra are no less interesting. The transition at approximately 38,000 cm^{-1}, with vibrational structures, and the intense peak at 40,320 cm^{-1} are assigned respectively to the intraligand charge transfer (i) $\pi \rightarrow \pi^*$ ($^1A_{1g} \rightarrow {}^1B_{2u}$ of benzene) and (ii) charge transfer involving perhaps the lone pair on arsenic and the benzene ring,[23] because of the identity of the results of free ligand with that of the complex. However, another band occurring at 45,250 cm^{-1} can be of M → L or L → M origin, possibly L being triphenylarsine. Since the complex I has magnetic and spectral properties identical with those of II, all what has been said above must also be applicable to the former in spite of its lower symmetry.

The most interesting part of the discussion centers around III, $RuCl_3(AsPh_3)_2$. The easy removal of coordinated methanol seems to be correct because I forms an acetone adduct $RuCl_3(AsPh_3)_2(CH_3)_2CO$ on being placed in acetone solvent.[5] Here acetone just displaced the coordinated methanol substituting itself in the place of methanol. However, in fairly inert solvents like benzene, methanol must just be lost. The epr results of III in solid form are close to those of complexes I and II with $g_\parallel$ around 1.73 and $g_\perp$ around 2.41 indicating that there has not been any gross change in either its molecular or electronic structure from those of I and II. We were unable to obtain a good electronic spectrum of this compound in the solid form. However, the epr spectrum in benzene or isooctane solutions with $g_\parallel = 2.00$ and $g_\perp = 2.48$ and an isotropic g value of 2.32 is quite different from that of III in solid or I and II, revealing that III has undergone a drastic structural change on dissolution in a noncoordinating solvent like benzene. Another obvious piece of evidence is the completely different electronic spectra of III in benzene-isooctane solutions. When this infomation is combined with the zero dipole moment of this compound in benzene solutions at different concentrations, the only reasonable structure consistent with the above properties is that of a trigonal bipyramid (TBP) with three chlorines in the equatorial plane and two triphenylarsine molecules along the z axis.

Such a prediction of a TBP structure on the basis of dipole moment data is not new since the zero dipole moment of $CoCl_3(P(C_2H_5)_3)_2$ in pentane solution had been taken as evidence for assigning a TBP structure.[24] However, the TBP structure for a d^5 configuration is rare since most of the TBP molecules occur in any one of the following configurations:[25] d^0, d^8, and d^{10}. The more or less identical epr results of I, II, and III (solid) indicates that the solid form of $RuCl_3(AsPh_3)_2$ can be given the square-pyramidal structure (C_{2v}), *i.e.*, the axial chlorine of one molecule is probably loosely coordinated to the sixth otherwise empty coordination site of the next molecule, thereby providing a geometry closely resembling that of II leading to similar anisotropic g values. In addition, such a stacking arrangement would involve a tremendous amount of exchange interaction, the presence of which is identified in the solid because the epr line widths for this solid turn out to be very high as compared to those of I and II, in spite of identical g values. When the solid is placed in a solvent, the loose binding between the adjacent molecules may be broken, necessitating a readjustment in the molecular geometry. It is worth pointing out here that the solution containing TBP molecule on evaporating gives back the original solid III which was identified from their g values.

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The one-electron ordering given in Figure 7, $e'' < a_1' < e'$, is justified on the basis of g values of the frozen glass of the TBP molecule. The experimental $g_\parallel$ value of 2.00 for this molecule in solution leaves no alternative but to place the unpaired spin on the d_{z^2} orbital since $\hat{L}_z |d_{z^2}\rangle = 0$ predicts a free-electron value for $g_\parallel$. The ground state of the molecule is, therefore, justified as ${}^2A_1'$. An attempt has been made to identify the excited states and their energies, on the basis of a crystal field model wherein the energies of the excited states given in Table IV are described in terms of crystal field parameters Ds, Dt, and Slater-Condon energies. Transitions below 30,000 cm^{-1} are identified as ligand field bands. The first (low-energy) band at 12,880 cm^{-1} is assigned to a one-electron transition from $e''(xz, yz)$ to $a_1'(z^2)$, *i.e.*, ${}^2A_1' \rightarrow {}^2E''$. That this assignment of the first band to this forbidden transition is correct can be proved by its lower extinction coefficient value (540) as compared to those (2400-6500) of allowed ones. Moreover, a more convincing proof for this assignment comes from the analysis of the $g_\perp$ values. A simple expression for $g_\perp$ for TBP molecule can be derived as

$$g_\perp = 2.0023\left(1 - \frac{3\lambda}{\Delta_\perp}\right)$$

where $\Delta_\perp$ represents the transition energy $e''(xz, yz) \rightarrow a_1'(z^2)$. Assuming $\lambda = -1000$ cm^{-1} for Ru^{3+} complexes[17,21,22] (λ is negative in sign) and $\Delta_\perp = 12{,}880$ cm^{-1}, we calculate $g_\perp = 2.47$ as against the experimental value of 2.48, which is an excellent agreement. Assigning this band to any other transition would greatly reduce the calculated value for $g_\perp$. In fact, the very accurate fitting of the experimental anisotropic g factors with the measured optical spectral data and the much used spin-orbit coupling constants are good support for (i) the transition under consideration being of crystal field origin, though forbidden in nature, and (ii) the molecule definitely having trigonal-bipyramidal geometry. It is to be remembered here that the λ value for the free ion[26] is of the order of 1250 cm^{-1}. The reduced λ value indicates that the covalency is fairly large in the TBP molecule.

The band at 18,350 cm^{-1} is assigned to the allowed transition $a_1'(z^2) \rightarrow e'(x^2 - y^2, xy)$, *i.e.*, ${}^2A_1' \rightarrow {}^2E'$. The remaining two closely spaced bands at 24,390 and 27,770 cm^{-1} are assigned to allowed excited states ${}^2A_2''$(I) and ${}^2A_2''$(II), arising out of the electronic configuration, $(e'')^3(a_1')^1(e')^1$. On the basis of the assignment of these transition energies, we were able to calculate the crystal field parameters Ds, Dt, and Slater-Condon energies F_2 and F_4. The calculated F_2/F_4 ratio of 9.96 is close to what has been predicted for ruthenium complexes[17] and $F_2 = 10F_4 = 1280$ cm^{-1} is quite a reasonable number. A comment is probably needed on the values of Ds and Dt. A comparison with the values from earlier work on trigonal-bipyramidal molecules[9,27,28] could not be made, since most of the work deals with high-spin first-row transition metal ions, while the case under consideration here is a second-row ion with a low-spin d^5 configuration.

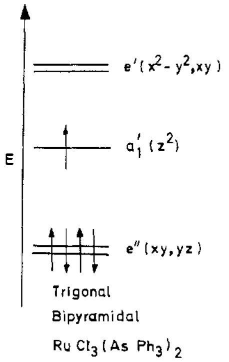

Figure 7. One-electron energy levels for the trigonal-bipyramidal molecule $RuCl_3(AsPh_3)_2$.

The next two high-energy absorption bands of the TBP molecule are identified as intraligand charge-transfer bands due to triphenylarsine. The band due to the $\pi \rightarrow \pi^*$ transition of the free ligand has moved to higher energy (approximately 2000 cm^{-1}) in the TBP complex and has better resolved fine structures on it. However, the other band occurring at 40,320 cm^{-1} in the isooctane solution of the free ligand has undergone a bathochromic shift of nearly 4000 cm^{-1} in the spectrum of the TBP molecule. These large shifts may be indicative of possible conjugation between arsenic and benzene rings through dπ-pπ interactions. Nothing certain can be said about the assignment of a third high-energy band at 48,080 cm^{-1} of the complex. Such a band was not observable in the free ligand and hence it may be due to M → L or L → M charge-transfer transition or due to the red-shifted ${}^1A_{2g} \rightarrow {}^1E_{1u}$ transition of benzene[29] as a result of complexing. In order to have a better understanding of the various aspects of this complex, further work in the area of molecular orbital calculation and detailed epr studies are under way.

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Registry No. $RuCl_3(CH_3OH)(AsPh_3)_2$, 37561-87-8; $N(C_2H_5)_4[RuCl_4(AsPh_3)_2]$, 28688-60-0; *SP*-$RuCl_3(AsPh_3)_2$, 41685-48-7; *TBP*-$RuCl_3(AsPh_3)_2$, 41685-49-8.

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