of $(+)_{546}Co(acac)_2en^+$ and $(+)_{546}Co(acac)_2(NH_3)_2^+$. This may be a consequence of the mixing of the charge-transfer and ligand states.

There is an interesting difference in the ultraviolet CD between cobalt(III) complexes of the same absolute configuration with one acetylacetonate chelate and those containing two chelates. It appears that the sign of the $d\pi \rightarrow \pi^*$ CD found at $\sim$30 kK is negative for all the $\Delta(C_2)$ complexes with one, two, or even three β-diketone chelates. Conversely, the charge-transfer CD band, at 40 kK, shows a reversal of sign, negative to positive, in going from $(+)Co(en)_2acac^+$ to $(+)_{546}Co(acac)_2en^+$. The ultraviolet CD spectra of mixed complexes of acetylacetone and ethylenediamine could also be complicated by the presence of ethylenediamine chelate charge-transfer bands in the 40–45-kK region.[28] However, the similarity of the ultraviolet CD spectra for $(+)_{546}Co(acac)_2(NH_3)_2^+$ and $(+)_{546}Co(acac)_2en^+$ indicates that the spectral difference noted above is mainly a function of the presence of two acetylacetonate chelate rings.

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The Spectra of Bis(tertiary arsine) Complexes. II. Spin-Paired Iron(III)[1a]

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New spin-paired compounds of iron(III) have been prepared and their visible spectra and magnetic properties examined. The spectral properties of the complexes tris[*cis*-1,2-bis(dimethylarsino)ethylene]iron(III), tris[*o*-phenylenebis(dimethylarsine)]iron(III), and tris(8-dimethylarsinoquinoline)iron(III) were compared with those of the corresponding complexes of α,α'-bipyridyl and *o*-phenanthroline. All of the compounds examined have one unpaired electron per iron(III) and their visible spectra can be interpreted on the basis of a ligand field model.

Introduction

The iron complexes with *o*-phenylenebis(dimethylarsine) (das) have been the subject of several previous studies.[2-4] The magnetic properties of the iron(III) complexes have received particular attention because they are all spin paired with $^2T_2$ ground states. The only other common spin-paired complexes of iron(III) are formed with strong-field ligands including cyanide, *o*-phenanthroline,[5] α,α'-bipyridyl,[6] dithiocarbamates,[7] etc. Of these iron(III) complexes, only the cyanide[8] and, more recently, the ethylenediamine complexes[9] have had their spectral properties examined in any detail. Since the ligand field spectra of many complexes of *o*-phenylenebis(dimethylarsine) and *cis*-1,2-bis(dimethylarsine)ethylene (edas) are by now rather well understood,[1a,10,11] it was of interest to examine the d–d transitions of the iron(III) complexes with these ligands. The results of these investigations are outlined below.

Experimental Section

Materials.—The ligands *o*-phenylenebis(dimethylarsine) and *cis*-bis(dimethylarsino)ethylene were prepared according to the methods described in the literature.[11,12] The compounds *o*-phenanthroline and α,α'-bipyridyl purchased from G. F. Smith and Co. were used without further purification. The perchlorate salts of the iron(III) complexes of *o*-phenanthroline and α,α'-bipyridyl, were prepared directly from these ligands using well-known procedures.[2,13]

Tris[*o*-phenylenebis(dimethylarsine)]iron(III) Perchlorate.—This complex was prepared from $Fe(das)_3^{2+}$ by oxidation[10] in concentrated nitric acid. Numerous attempts were made to prepare the pure solid. Although the complex is readily prepared in solution, it proved difficult to obtain this solid compound in reproducible yields. The following procedure represents the best preparation thus far found.

The ferrous complex $[Fe(das)_3][ClO_4]_2$ (1 g) was dissolved in a minimum (25 ml) of concentrated nitric acid. The resultant

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Table I

Temperature Dependence of the Magnetic Susceptibility of Spin-Paired d^5 Complexes

	$[Fe(edas)_3][ClO_4]_3$								$[Fe(o\text{-}phen)_3][ClO_4]_3$	$[Fe(\alpha,\alpha'\text{-}bipy)_3][ClO_4]_3$	$[Fe(asq)_3][ClO_4]_3$
Temp, °K	291.6	249.7	195.0	165.6	135.4	124.0	107.1	77.1	300	300	297
$10^6M'$	2766	2929	3434	3978	4507	4647	5031	7009	1910	1900	2149
μ_{eff}	2.54	2.42	2.31	2.31	2.21	2.15	2.08	2.08	2.40	2.40	2.27

dark green solution was evaporated to 10 ml on a steam bath. A saturated solution of sodium perchlorate in water was then added dropwise until a white precipitate formed and dissolved on shaking. The solution was then cooled until the solution began to freeze. After allowing the solution to warm to room temperature, the resultant impure green crystals were removed by filtration and discarded. The above process was repeated (boiling, cooling, and filtering) until a third crop of large, well-formed dark green crystals was obtained. *Anal.* Calcd for $[Fe(C_6H_4(As(CH_3)_2)_2)_3][ClO_4]_3$: C, 29.7; H, 4.0. Found: C, 31.6; H, 5.4. (The sample exploded and consequently there is a large experimental error.)

Tris[*cis*-1,2-bis(dimethylarsino)ethylene]iron(III) Perchlorate.—The procedure for the preparation of this complex was similar to that used for the *o*-phenylenebis(dimethylarsine) complex reported above, with the exception that the iron(III) complex of *cis*-1,2 bis(dimethylarsino)ethylene is much more easily isolated. Once prepared, this complex is stable indefinitely when sealed from the air. The compound[11] $[Fe(edas)_3][ClO_4]_2$ (1 g) was dissolved in 25 ml of concentrated nitric acid, and 5 ml of dilute $NaClO_4$ solution (1 *M*) was added. The solution was then evaporated to approximately 5 ml on a hot plate. The dark green product precipitated (0.45 g) and was collected by filtration. After washing with water, the crystalline product was dried at 60° under vacuum for 2 days. *Anal.* Calcd for $[Fe(C_2H_2(As(CH_3)_2)_2)_3][ClO_4]_3$: C, 20.4; H, 4.10; Cl, 10.0. Found: C, 20.9; H, 4.0; Cl, 9.9.

Tris(8-dimethylarsinoquinoline)iron(III) Perchlorate.—The complex $Fe(asq)_3(ClO_4)_2$ (0.45 g) was dissolved in 13 ml of cold concentrated nitric acid. The solution was filtered, and 3 ml of a saturated solution of $NaClO_4$ was added to precipitate the dark green product. The product was redissolved in concentrated nitric acid and reprecipitated with sodium perchlorate several times, until a pure product was obtained. The resultant dark green complex was washed with a little water, alcohol, and finally ether. After drying for several days under vacuum, the following analyses were obtained. *Anal.* Calcd for $[Fe(C_9H_6NAs(CH_3)_2)_3][ClO_4]_3$: C, 37.6; H, 3.4; Cl, 10.1; N, 4.0. Found: C, 34.7; H, 3.9; Cl, 10.8; N, 4.3. (The sample exploded and consequently there is a large experimental error.)

Physical Measurements.—The solution spectra were obtained using a Cary Model 14. The reflectance spectra were measured using a Zeiss PMQ II with a specially built PbS detector for measurements for 4.0–17 kK. The reflectance spectra were subjected to gaussian analysis by means of a Du Pont curve resolver, Model 310. The magnetic susceptibilities of these complexes were measured from 77 to 300°K using a Faraday balance similar to that described by Hatfield.[14]

Results and Discussion

There are three spin multiplets which are possible for the ground state of iron(III) complexes. In complexes with octahedral symmetry,[15] iron(III) complexes can only have a spin $S = {}^1/_2$ or $S = {}^5/_2$. Iron(III) complexes in fields of tetragonal symmetry or lower can have a quartet ground term with $S = {}^3/_2$ as well. For octahedral d^5 complexes, the requirements for spin pairing are that $10Dq$ (Δ) be greater than the spin-pairing energy, which for iron(III) is estimated to be 28 kK from the values of *B* and *C* for the free ion. The values of Δ which had been previously obtained for *o*-phenylenebis(dimethylarsine) and *cis*-1,2-bis(dimethylarsino)ethylene[1a,11] are approximately the same as obtained for ethylenediamine (en),[10] being near 21 kK for all three ligands. However, at the time this research was initiated, the complexes $Fe(en)_3{}^{3+}$ and $Fe(NH_3)_6{}^{3+}$ were reported to be spin free with a sextet ground state,[6] while the complexes $Fe(das)_3{}^{3+}$ and $Fe(edas)_3{}^{3+}$ had been found to be spin paired. One possible explanation of these results was that the interelectron repulsion (*B*) within the t_{2g} orbitals of the iron(III)–arsine complexes had been markedly reduced compared with the corresponding ethylenediamine complex, $Fe(en)_3{}^{3+}$. The reduction of the interelectron repulsion can be taken as one measure of covalency.[16] In the present case, the ratio of B_{as}/B_{en} should give a direct measure of the amount of delocalization of the t_{2g} electrons of iron(III) into the $d\pi$ orbitals of the arsenic ligands.

A subsequent report[9] has shown that $Fe(en)_3{}^{3+}$ is spin paired so that there is no longer a discrepancy between the magnetic ground states of $Fe(en)_3{}^{3+}$, $Fe(das)_3{}^{3+}$, and $Fe(edas)_3{}^{3+}$. However, a comparison of the ligand field parameters of $Fe(en)_3{}^{3+}$ with those of $Fe(das)_3{}^{3+}$ and $Fe(edas)_3{}^{3+}$ should give some indication of the degree of participation by the d orbitals of the arsenic in π bonding with the t_{2g} orbitals of the iron(III). Accordingly, the magnetic susceptibility and visible spectra of these spin-paired iron(III) complexes of ditertiary arsines has been examined in detail.

The magnetic susceptibility of $[Fe(edas)_3][ClO_4]_3$ has been obtained from 80 to 300°K. These data and the magnetic susceptibility at room temperature of the other Fe(III) compounds are reported in Table I. The magnetic susceptibility of $Fe(edas)_3{}^{3+}$ increases from a value of 2.08 BM at 80°K to 2.53 BM at room temperature. The temperature dependence of the magnetic moment of $Fe(edas)_3{}^{3+}$ follows that which is predicted[17] for a ${}^2T_{2g}$ ($t_{2g}{}^5$) ground state of Fe(III) and that found previously for $Fe(CN)_6{}^{3-}$ and $Fe(en)_3{}^{3+}$. Using a value for λ of -400 cm^{-1}, the magnetic susceptibility of Fe(III) with a ${}^2T_{2g}$ ground state is expected[17] to range from 2.0 BM at 80°K to 2.55 BM at 300°K. Although the present magnetic data are not sufficiently accurate to obtain the precise figures, the splitting of the ${}^2T_{2g}$ ground state by fields of lower symmetry is small. The ${}^2T_{2g}$ ground state in $Fe(CN)_6{}^{3-}$ has a measured splitting of approximately 100 cm^{-1} while both $Fe(bipy)_3{}^{3+}$ and $Fe(phen)_3{}^{3+}$ have larger ground-state splittings of 600 cm^{-1}. An

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TABLE II
THE ELECTRONIC SPECTRA OF THE SPIN-PAIRED IRON(III) COMPLEXES

Compound	ν, kK					
	$^4T_1$	$^4T_2$	$^2T_1$, $^2A_2$	$^2T_2$	^2E	$^2T_1$, $^2T_2$
$[Fe(edas)_3][ClO_4]_3$	9.0 (8.7)[a]	12.5 (12.7)	15.7 (15.9)	17.4 (17.9)	19.5 (19.3)	23.5 (23.5)
$[Fe(das)_3][ClO_4]_3$[c]	... (8.7)	... (12.7)	15.7 (15.9)	17.5 (17.9)	19.5 (19.3)	23.5 (23.5)
$[Fe(asq)_3][ClO_4]_3$	8.5 (8.7)	... (12.7)	16.0 (15.9)	17[b] (17.9)	19.6 (19.3)	23.4 (23.5)
$[Fe(bipy)_3][ClO_4]_3$	9.3 (9.5)	14[b] (13.5)	16.0 (16.6)	17.3[b] (18.6)	... (20.0)	24.5[b] (24.2)
$[Fe(o\text{-phen})_3][ClO_4]_3$	9.7 (9.5)	14[b] (13.5)	16.3 (16.6)	18.7 (18.6)	... (20.0)	24.0 (24.2)

[a] The numbers in parentheses are calculated values. [b] Unresolved shoulders. [c] Solution spectrum.

upper limit of 800 cm^{-1} for the splitting of the $^2T_{2g}$ term can be set from the maximum and minimum values of the magnetic moment of $Fe(edas)_3^{3+}$.

The spin-paired complexes of iron(III) are well known to be rather unstable and easily reduced to iron(II) complexes. The perchlorate salts of $Fe(das)_3^{3+}$, $Fe(edas)_3^{3+}$, $Fe(asq)_3^{3+}$, $Fe(phen)_3^{3+}$, and $Fe(bipy)_3^{3+}$ were obtained from the iron(II) complexes by dissolving the ferrous complexes in concentrated nitric acid and precipitating the iron(III) complex by the addition of perchlorate acid and sodium perchlorate. These salts are decomposed in all solvents other than nitric acid. Consequently, the absorption spectra could only be measured in concentrated nitric acid. The reflectance spectra of the pure solids were also obtained and were in good agreement with those spectra obtained from solutions of iron(III) complexes in concentrated nitric acid. The reflectance and solution spectra are reported in Table II. The spectra of all complexes in Table II are very similar. Two transitions of rather low intensity have been observed in the region from 9 to 13 kK. These absorption bands were readily distinguished from combination and overtones of the ligands by their large band width, by comparison with other complexes of these ligands, and finally by the fact that their presence is independent of the ligand. From their low extinction coefficients, they have been indentified as the spin-forbidden transitions from the $^2T_{2g}$ ground state to the $^4T_1$ and $^4T_2$ excited states, respectively. The first spin-allowed transition is found near 16 kK in all of the complexes—$Fe(edas)_3^{3+}$ (Figure 1), $Fe(das)_3^{3+}$, $Fe(asq)_3^{3+}$, (Figure 2) $Fe(phen)_3^{3+}$, and $Fe(dipy)_3^{3+}$. In addition to this transition, a shoulder is observed at higher energies at approximately 18 kK. This shoulder is not resolved in all of these compounds, but its position can be determined by gaussian analysis in those cases in which it is poorly defined. A third spin-allowed transition is found in these complexes near 19 kK, while the final absorption band, identifiable as a d–d type transition, occurs as a shoulder near 23 kK.

The energy level expressions including configuration interaction for Fe(III) in a strong octahedral field are easily derived using the methods of Griffith.[16] These levels and their relative energies are given in Figure 3. Using the order of energy levels given in Figure 3, the observed electronic transitions can be assigned for $Fe(edas)_3^{3+}$. From their position and their low intensities, the two very weak transitions near 9 and 13 kK can be assigned to the two spin-

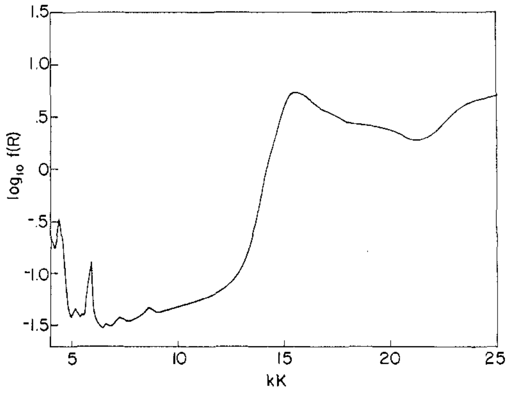

Figure 1.—The reflectance spectrum of $[Fe(edas)_3][ClO_4]_3$.

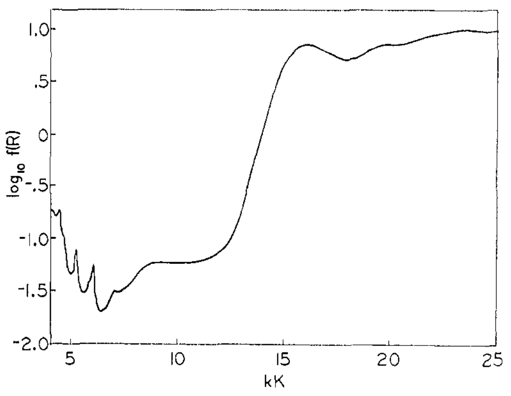

Figure 2.—The reflectance spectrum of $[Fe(asq)_3][ClO_4]_3$.

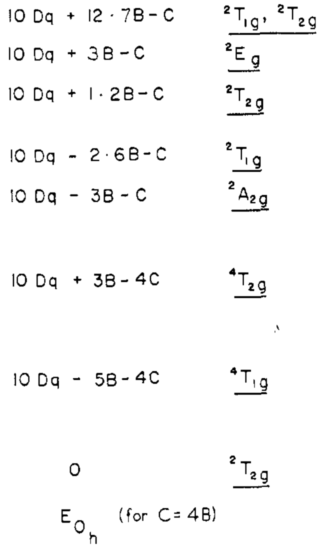

Figure 3.—The energy level expressions with configuration interaction for a d^5 ion in a strong octahedral field.

forbidden transitions $^2T_2 \rightarrow {}^4T_1$ and $^2T_2 \rightarrow {}^4T_2$. Without further investigation, the spin-allowed transitions cannot be unambiguously assigned. Tentatively, the following assignments are consistent with the present data and the calculations discussed below: $^2T_2 \rightarrow {}^2T_1, {}^2A_2$ at 15.6 kK, $^2T_2 \rightarrow {}^2T_2$ at 17.2 kK, $^2T_2 \rightarrow {}^2E$ at 19.2 kK, and $^2T_2 \rightarrow {}^2T_1, {}^2T_2$ at 23.5 kK.

While the complex of 8-dimethylarsinoquinoline formally has symmetry lower than octahedral, the nitrogen donor atom and the arsenic donor atom have effectively similar ligand fields (compare *o*-phenanthroline with *o*-phenylenebis(dimethylarsine)). If there is splitting of the octahedral states, it could not be observed. Splitting of these octahedral states can be observed in the tetragonal complexes, *trans*-$FeX_2(das)_2^+$. The results of the spectral investigations of these tetragonal complexes will be discussed in a later paper.

The intensities of these transitions deserve further comment. The transitions in the visible spectra of $Fe(bipy)_3^{3+}$ and $Fe(phen)_3^{3+}$ have previously been identified as charge-transfer bands, since they have rather high molar extinction coefficients.[18,19] However, when the absorptivity is apportioned among the transitions which contribute to the total absorption of these Fe(III) compounds, then the maximum value of ϵ found for the individual transitions is no more than 340 M^{-1} cm^{-1}. These are rather high values for d–d transitions but are within the range found for transition metal–arsine complexes.[1a]

Of equal importance, if these were charge-transfer transitions from the σ or π orbitals of the ligands to the d orbitals of the Fe(III) as has been previously suggested, the position of these transitions should be quite sensitive to changes in the σ and π orbitals of the ligands. The transitions in the visible region of the spectrum for all of the Fe(III) complexes examined in this research are relatively insensitive to drastic changes in the σ and π orbtials of the ligands (substitution of an As for N and a phenanthroline π system for that of *o*-phenylenebis(dimethylarsine)).

Values of *Dq*, *B*, and *C* for the Cr(III) and Co(III) complexes have been obtained previously.[1a] Using the values form the Cr(III) compounds as estimates for the $Fe(edas)_3^{3+}$ parameters, a reasonable fit of the observed spectrum can be obtained using the energy expressions in Figure 2. The values of *Dq*, *B*, and *C* which give the best fit of the spectral data for the compounds $Fe(edas)_3^{3+}$, $Fe(das)_3^{3+}$, $Fe(asq)_3^{3+}$, $Fe(phen)_3^{3+}$, and $Fe(bipy)_3^{3+}$ are given in Table III. As has been previously noted,[1a] the values of *Dq* obtained for complexes of *o*-phenylenebis(dimethylarsine), *cis*-1,2-bis(dimethylarsino)ethylene, and ethylenediamine are closely similar, while the values of *B* and *C* are ordinarily less for the chelating arsenic ligands than for ethylenediamine. The value of *B* for $Fe(edas)_3^{3+}$ is somewhat larger than was found previously for $Fe(edas)_3^{2+}$. This is to be expected, since the increased nuclear charge of Fe(II) to Fe(III) should serve to increase the interelectron repulsion between d electrons. The value of *Dq* for the *o*-phenylenebis(dimethylarsine) complexes fall in the order: Co(III) > Fe(II) > Cr(III) > Fe(III). This order parallels the qualitative order of reactivity which has been observed for these complexes.

TABLE III
LIGAND FIELD PARAMETERS FOR
SPIN-PAIRED IRON(II) COMPLEXES

Compound	$10Dq$, kK	B/B_0[a]	B, cm^{-1}	C, kK	C/B
$[Fe(edas)_3][ClO_4]_3$	19.4	0.49	500	2.05	4.01
$[Fe(das)_3][ClO_4]_3$	19.4	0.49	500	2.05	4.01
$[Fe(asq)_3][ClO_4]_3$	19.4	0.49	500	2.05	4.01
$[Fe(o\text{-phen})_3][ClO_4]_3$	20.0	0.49	500	2.00	4.00
$[Fe(\alpha,\alpha'\text{-bipy})_3][ClO_4]_3$	20.0	0.49	500	2.00	4.00
$[Fe(en)_3]_3[ClO_4]_3$	19.5	0.49	500	2.00	4.00

[a] B_0 for the free ion was taken as 1015 cm^{-1}.

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