posited was recrystallized from hot water; yield 0.3 g. *Anal.* Calcd for $Ni(C_{13}H_{12}N_2S)_2(ClO_4)_2$: Ni, 8.2; C, 43.7; H, 3.4; N, 7.8; S, 9.0. Found: Ni, 8.0; C, 43.1; H, 3.4; N, 7.6; S, 8.8.

Preparation 2.—Bis(N-2-thiolophenyl-2′-pyridylmethylenimine)nickel(II) (0.5 g) was suspended in hot alcohol (45 ml) containing lithium perchlorate trihydrate (1 g). Methyl iodide (5 ml) was added to the hot solution which was then shaken in a sealed flask. The crude brown product (0.6 g) was recrystallized from water and then from an acetone–water mixture; yield 0.2 g. *Anal.* Found: Ni, 8.0; C, 44.1; H, 3.6; N, 7.9.

Preparation 3.—N-2-Methylthiophenyl-2′-pyridylmethylenimine (0.15 g) in alcohol (10 ml) was added to nickel perchlorate hexahydrate (0.1 g) in alcohol (10 ml). The solution was let stand and brown crystals of the product deposited; yield 0.1 g. *Anal.* Found: C, 43.55; H, 3.5; N, 7.65.

Preparation 4.—Preparation 3 was repeated except that the formation of the ligand (0.15 g) from 2-pyridinecarboxaldehyde and 2-aminobenzenethiol was carried out in the presence of the nickel perchlorate hexahydrate (0.1 g) in hot alcohol; yield 0.1 g. *Anal.* Found: Ni, 8.2; C, 42.9; H, 3.6.

Reaction of γ-Picoline with Diiodobis(2-methylthioaniline)nickel(II).—Diiodobis(2-methylthioaniline)nickel(II) (0.4 g) was dissolved in hot acetone (400 ml) containing γ-picoline (5 ml). On cooling, the solution deposited bright green crystals of diiodotetrakis(γ-picoline)nickel(II); yield 0.2 g. *Anal.* Calcd for $Ni(C_6H_7N)_4I_2$: Ni, 8.6; C, 42.1; H, 4.1; N, 8.2. Found: Ni, 8.7; C, 42.1; H, 4.1; N, 8.1. Loss on heating to 140°: 27.2%. Calcd loss of two γ-picoline molecules: 27.0%.

Reaction of γ-Picoline with Bis(2-aminobenzenethiolo)nickel(II).—Finely ground bis(2-aminobenzenethiolo)nickel(II) (0.4 g) was suspended in alcohol (100 ml) containing γ-picoline (6 ml) and lithium iodide (1 g). This suspension was refluxed for 5 hr and then filtered. The green residue (0.3 g) was discarded and the filtrate was concentrated, treated with charcoal, and let stand. Bright green crystals of diiodotetrakis(γ-picoline)nickel(II), identical with those obtained in the previous preparation, deposited. *Anal.* Found: Ni, 9.0; C, 43.3; H, 4.3; N, 8.1.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF ARIZONA, TUCSON, ARIZONA 85721

The Spectra of Bis(tertiary arsine) Complexes

BY ROBERT D. FELTHAM AND W. SILVERTHORN[1]

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The visible and near-infrared spectra of several complexes of Cr(III), Co(III), and Fe(II) with the ligand *o*-phenylenebis(dimethylarsine) have been obtained both in solution and in the solid state. The electronic transitions which were observed were found to be d–d transitions and were assigned on the basis of a ligand field model. An evaluation of the ligand field parameters, Dq, B, and C, for these compounds indicates that there is a considerable amount of σ bonding between the metal ions and *o*-phenylenebis(dimethylarsine) but that there is no evidence for $d\pi$–$d\pi$ bonding between the metal and the ligand in these complexes.

Introduction

The ligand *o*-phenylenebis(dimethylarsine) (das) is one of the most versatile complexing agents known. After the initial investigations of Chatt and Mann,[2] Nyholm and his coworkers[3] have succeeded in preparing compounds of *o*-phenylenebis(dimethylarsine) with almost every transition metal (excluding the lanthanides and actinides). These compounds include complexes in which the coordination number of the metal is 4, 5, 6, 7, and 8 and in which the oxidation number of the metal ranges from 0 in $Ni(das)_2$ to 5 in $ReX_4(das)_2^+$. However, the factors which are responsible for the extraordinary coordinating power of this ligand and the stability of these complexes remain obscure. The present research was initiated in an attempt to elucidate some of these factors.

Although transition metal complexes of *o*-phenylenebis(dimethylarsine) have been known for over 25 years, there have been only three papers which have dealt with their spectroscopic properties in any detail.[4–6] It is well known that *o*-phenylenebis(dimethylarsine) is a "strong-field" ligand, since most of its complexes are spin paired. The spectrum and magnetism of the complex $Ni(das)_3^{2+}$ have been interpreted on the basis of a molecular orbital model with a trigonal electric field.[5] The spectra of the cobalt(III) compounds $CoX_2(das)_2^+$ have been shown to be consistent with a ligand field model with tetragonal symmetry,[4] but only one d–d transition was observed. The reflectance and solution spectra of the *o*-phenylenebis(dimethylarsine) complexes of Co(III), Fe(II), and Cr(III) are reported and discussed below.

Experimental Section

Materials and Analyses.—The ligand *o*-phenylenebis(dimethylarsine) and its complexes were prepared according to the methods described in the literature.[7–11] In several instances, the compounds were reported to exist, but neither elemental analyses nor details for their preparation were reported. The

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[1] Shell Research Fellow, 1966–1967.

[2] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 610 (1939).

[3] For a summary of many of these complexes, see "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., 1964, Chapter 3.

[4] T. M. Dunn, R. S. Nyholm, and S. Yamada, *J. Chem. Soc.*, 1564 (1962).

[5] B. Bosnich, R Bramley, R. S. Nyholm, and M. L. Tobe, *J. Am. Chem. Soc.*, **88**, 3926 (1966).

[6] S. Yamada, *Coord. Chem. Rev.*, **2**, 83 (1967).

[7] R. D. Feltham, A. Kasenally, and R. S. Nyholm, *J. Organometal. Chem.* (Amsterdam), **7**, 285 (1967).

[8] R. S. Nyholm, *J. Chem. Soc.*, 2070 (1950).

[9] R. S. Nyholm and G. J. Sutton, *ibid.*, 560 (1958).

[10] R. S. Nyholm and G. J. Sutton, *ibid.*, 567 (1958).

[11] F. H. Burstall and R. S. Nyholm, *ibid.*, 3570 (1952).

detailed preparations for these compounds are described in this section. The compounds were analyzed for C, H, O, As, and halogen by Huffman Laboratories, Wheatridge, Colo.

Dihalobis[*o*-phenylenebis(dimethylarsine)]chromium(III) Perchlorates.—The chloride, bromide, and iodide were prepared according to Nyholm.[9] However, the iodide prepared by Nyholm was stated to be pale green. The material obtained in the present research was found to be yellow-brown and is isomorphous with the other halides (Table I). A pale green material was also obtained from this preparation, but it was found to contain no *o*-phenylenebis(dimethylarsine).

TABLE I

ELEMENTAL ANALYSES

Compound	Color	% calcd		% found	
		C	H	C	H
$[Fe(das)_3][ClO_4]_2$	Orange	32.4	4.4	32.1	4.5
$[FeBr_2(das)_2]$	Yellow	30.7	4.1	30.6	4.4
$[FeI_2(das)_2]$	Yellow	27.4	3.7	29.0	4.1
$[CoCl_2(das)_2][ClO_4]$	Green	30.0	4.0	31.0	4.3
$[Co(das)_3][ClO_4]_3$	Yellow	29.7	4.0	29.8	4.1
$[CrCl_2(das)_2][ClO_4]$	Green	30.4	4.1	31.0	4.2
$[CrBr_2(das)_2][ClO_4]$	Green	27.3	3.7	28.2	3.9

Dihalobis[*o*-phenylenebis(dimethylarsine)]cobalt(III) Perchlorates.—These compounds were identified by their absorption spectra which have been reported earlier.[4]

Tris[*o*-phenylenebis(dimethylarsine)]cobalt(III) Perchlorate.—This compound was prepared using the method of Burstall and Nyholm.[11] The compound was washed with ethanol and dried at 100° under vacuum; the elemental analyses are reported in Table I.

Tris[*o*-phenylenebis(dimethylarsine)]iron(II) Perchlorate.—Ferrous perchlorate (1.2 g) in 40 ml of methanol was treated with 3.0 g of *o*-phenylenebis(dimethylarsine). After refluxing for several hours, the orange complex was removed by filtration, washed with ethanol, and dried at 60° under vacuum (Table I).

Dihalobis[*o*-phenylenebis(dimethylarsine)]iron(II).—The chloro, bromo, and iodo compounds were prepared from the anhydrous halide and *o*-phenylenebis(dimethylarsine) in alcohol under nitrogen according to the methods of Nyholm[7] (Table I).

Physical Measurements.—The solution spectra were obtained using a Cary Model 14. The reflectance spectra were measured using a Zeiss Model PMQ II with a specially built PbS detector for measurements from 4.0 to 17 kK. The X-ray photographs were obtained using a Philips powder camera 11.48 cm in diameter.

Results

The d^6 Complexes.—The complexes of Fe(II) and Co(III) with *o*-phenylenebis(dimethylarsine) are all diamagnetic. The compounds $[Co(das)_3][ClO_4]_3$ and $[Fe(das)_3][ClO_4]_2$ have been reported,[11] but their electronic spectra have not been described. The solution spectra of both *cis*- and *trans*-$CoX_2(das)_2^+$ have been studied,[4] but the spectra of $FeX_2(das)_2$ have not heretofore been reported.

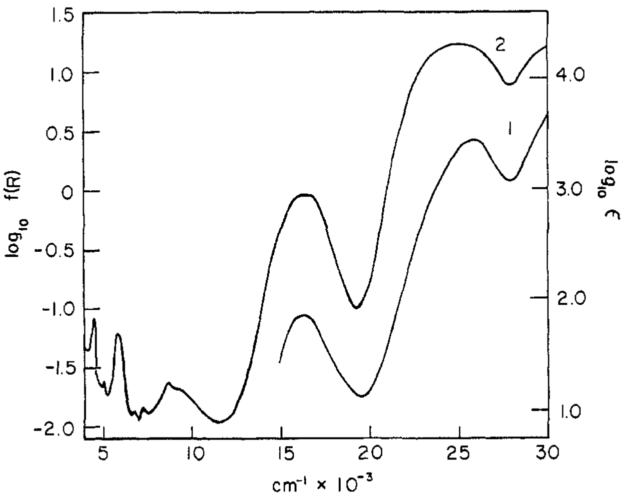

Figure 1.—The solution (1) and reflectance (2) spectra of *trans*-$[CoCl_2(das)_2][ClO_4]$.

The reflectance and solution spectra of *trans*-$[CoCl_2(das)_2][ClO_4]$ are shown in Figure 1. The solution spectrum of this Co(III) complex is identical with that obtained in ref 4 and is shown for comparative purposes. There are several features in the reflectance spectrum which are significant. The electronic transition in the pure solid near 16 kK is not shifted from the spectrum obtained in solution. Moreover, the relative intensity and general shapes of these solution and reflectance spectra are the same for this compound and for all of the other compounds in this series. The very weak and sharp absorption bands between 4 and 9 kK in the reflectance spectrum of $[CoCl_2(das)_2][ClO_4]$ are present in all of the complexes of *o*-phenylenebis(dimethylarsine). These absorption bands were identified as vibrational overtone and combination bands from the transmission spectrum of pure *o*-phenylenebis(dimethylarsine). These ligand absorptions are readily distinguished from the electronic transitions by the facts that they are much narrower and their position is not dependent upon the metal to which the ligand is attached. The broad, weak transition at 9.2 kK is an electronic transition of the cobalt complex and from its position and relative intensity must be a spin-forbidden transition of Co(III).

The spectra of the tetragonal Fe(II) complexes which are also spin paired and diamagnetic are listed in Table II along with the spectra of the Co(III) complexes. These tetragonal complexes have been discussed elsewhere,[12] but the spectra are presented here in order to identify the ligand absorptions and to establish the reliability of the reflectance measurements on these compounds.

The spectra of $[Co(das)_3][ClO_4]_3$ and $[Fe(das)_3][ClO_4]_2$ are illustrated in Figure 2. The general features of the spectra of these two compounds are very similar. The first spin-forbidden transitions in these octahedral d^6 complexes are near 15 kK, while the first spin-allowed transition is near 21 kK. The Fe(II) complex is of particular importance since in this case two spin-allowed transitions can be identified with certainty, the second occurring at 26.6 kK. The spectrum of $[Co(das)_3][ClO_4]_3$ has been reported previously,[6] incorrectly. The present authors have found that on standing, solutions of $[Co(das)_3][ClO_4]_3$ decompose to form *trans*-$CoCl_2(das)_2^+$. The spectrum reported in ref 6 has two absorption bands in the region between 20 and 28 kK. The absorption band at 23.2 kK corresponds to the first spin-allowed band of the $[Co(das)_3][ClO_4]_3$, while the additional absorption at 25 kK is due to the presence of *trans*-$CoCl_2(das)_2^+$. The spectrum of pure

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(12) T. M. Dunn and S. Yamada, private communication.

Table II

Electronic Spectra of the d^6 Complexes

	Absorption max, kK (ϵ_{max}, M^{-1} cm^{-1})				
	$^3T_1$		$^1T_1$		$^1T_2$
Compound	(^3E)	($^3A_2$)	(^1E)	($^1A_2$)	(^1E and $^1B_2$)
[Fe(das)$_3$][ClO$_4$]$_2$	14.5[a]		21.4	(230)[b]	26.6 (350)
trans-FeCl$_2$(das)$_2$	...	...	13.5[a]	22.4	25.5
trans-FeBr$_2$(das)$_2$	...	...	12.9[a]	22.5	26.0
trans-FeI$_2$(das)$_2$	...	...	12.7[a]	22.5	25.5
[Co(das)$_3$][ClO$_4$]$_3$	16.5		23.2	(600)[b]	...
trans-[CoCl$_2$(das)$_2$][ClO$_4$]	9.2	...	16.4	...	...
trans-[CoBr$_2$(das)$_2$][ClO$_4$]	...	...	15.7	...	...
trans-[CoI$_2$(das)$_2$][ClO$_4$]	...	...	15.2	...	...
Co(en)$_3{}^{3+}$	17.5		21.5		29.5
trans-CoCl$_2$(en)$_2{}^+$	...	...	16.1	22.5	25.9

[a] All of the spectra reported were obtained from the diffuse reflectance of the pure solids. [b] The extinction coefficients were obtained from 10^{-3} M solution in DMSO.

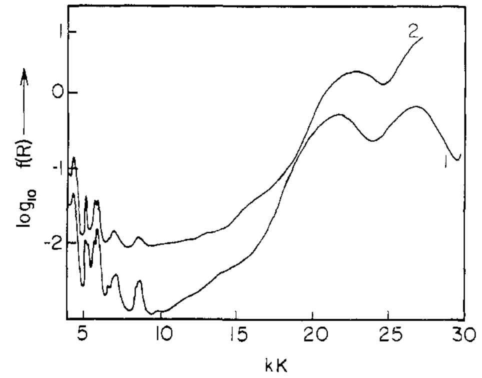

Figure 2.—The reflectance spectra of (1) [Fe(das)$_3$][ClO$_4$]$_2$ and (2) [Co(das)$_3$][ClO$_4$]$_3$.

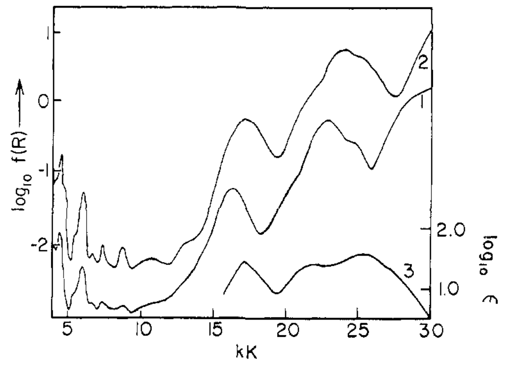

Figure 3.—The reflectance spectra of (1) *trans*-[CrBr$_2$(das)$_2$][ClO$_4$] and (2) *trans*-[CrCl$_2$(das)$_2$][ClO$_4$] and the solution spectrum of (3) *trans*-[CrCl$_2$(en)$_2$][ClO$_4$].

[Co(das)$_3$][ClO$_4$]$_2$ is reported in Table II. The second spin-allowed transition in the Co(III) complex is unfortunately obscured by an intense charge-transfer transition at 32 kK. The extinction coefficients are rather higher than those observed in amine and aquo complexes but are quite typical of those found for d–d transitions in other *o*-phenylenebis(dimethylarsine) complexes.[12]

The d^3 Complexes.—The chromium complexes, CrX$_2$(das)$_2{}^+$, have been prepared previously by Nyholm,[9] but the spectra of these complexes have not previously been reported. Unfortunately, it has thus far proved impossible to prepare the compound Cr(das)$_3{}^{3+}$. The *trans* stereochemistry of these chromium complexes was established by comparing the X-ray powder patterns of [CrCl$_2$(das)$_2$][ClO$_4$] and [CoCl$_2$(das)$_2$][ClO$_4$] which have been shown to have *trans* stereochemistry.[13] The reflectance spectrum of *trans*-CrCl$_2$(das)$_2{}^+$ and the solution spectrum of *trans*-CrCl$_2$(en)$_2{}^+$ are shown in Figure 3, while the electronic absorptions of all the chromium complexes are listed in Table III. The spectral features of these tetragonal d^3 complexes of Cr(III) are very similar to those of the tetragonal d^6 complexes discussed above. In these chromium complexes, the charge-transfer bands are displaced to higher energies, making it possible to observe additional d–d transitions.

Only the vibrational overtone and combination bands are observed between 4 and 10 kK (compare Figures 1 and 2), but the spectral region from 10 to 27 kK is very rich in electronic absorption bands. The first spin-forbidden transition can be identified near 13 kK and the first spin-allowed band is at 17.0 kK (Table III). Between 21 and 26 kK, there are three transitions. Although the extinction coefficients of the transitions at 25 kK are rather high, they are typical of extinction coefficients found in other arsine and phosphine complexes.[14] From Figure 3, it can be seen that the spectra of *trans*-CrCl$_2$(das)$_2{}^+$ and *trans*-CrCl$_2$(en)$_2{}^+$ differ mainly in the spectral region above 27 kK. In the arsine complex, a rather intense transition lies near the d–d transitions, while in the ethylenediamine complex, the d–d transitions are well separated from these bands with high molar extinction coefficients. These transitions with high molar extinction coefficients will not be considered further.

Discussion

The d^6 Complexes.—There are several features of importance in these spectra. First, three d–d transitions were observed for Fe(das)$_3{}^{2+}$, which from their positions and intensities are easily assigned as the transitions of an octahedral spin-paired d^6 complex. The first weak electronic transition which is observed for Fe(das)$_3{}^{2+}$ at 14 kK is the spin-forbidden transition

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(13) P. Pauling, Final Technical Report No. 1, University College, London, 1963, p 30.

(14) I. V. Howell, L. M. Venanzi, and D. C. Goodall, *J. Chem. Soc.*, 395 (1967).

TABLE III

ELECTRONIC SPECTRA OF THE d^3 COMPLEXES

	Absorption max, kK (ϵ_{max}, M^{-1} cm^{-1})				
	^2E, $^2T_1$	$^4T_2$		$^4T_1$	
Compound	($^2A_1$, $^2B_1$)	(^4E)	($^4B_2$)	($^4A_2$)	(^4E)
[$CrCl_2(das)_2$][ClO_4]	13.3[a]	17.0 (8.0)[b]	20.8 (270) sh	23.6 (1300)	25.5 (900) sh
[$CrBr_2(das)_2$][ClO_4]	13.3[a]	16.3 (140)[b]	20.0 (180) sh	22.6 (1150)	24.5 (670) sh
[$CrI_2(das)_2$][ClO_4]	13.3[a]	15.4 (100)[b]	...	...	...
$CrCl_2(en)_2^+$ [c]	14.4	17.3 (25.8)	22.0 (24.6) sh	25.3 (36.6)	26.9 (∼22) sh
$Cr(en)_3^{3+}$ [c]	15.0	21.9 (80)		28.5 (68)	

[a] Observed in reflectance only. [b] 5×10^{-4} *M* in acetone. [c] K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20,** 1603 (1964); J. R. Perumareddi, *J. Phys. Chem.*, **71,** 3155 (1967).

$^1A_1 \rightarrow {}^3T_1$, while the two more intense bands at 21.4 and 26.6 kK are the spin-allowed transitions $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$. From these assignments, it is possible to evaluate the ligand field parameters for this complex. The resultant values calculated using the well-known[15] energy expressions for an octahedral d^6 complex are $Dq = 2490$ cm^{-1}, $B_{35} = 325$ cm^{-1}, and $C = 3450$ cm^{-1}. This value of *Dq* places *o*-phenylenebis(dimethylarsine) above ethylenediamine ($Dq = 2320$ cm^{-1}) in the spectrochemical series. The value of *B* is remarkably reduced from the free-ion value of 890 cm^{-1} giving a value of $\beta_{35} = 0.36$ compared to a value of $\beta_{35} = 0.45$ in $Fe(CN)_6^{4-}$. This value represents either a reduction in the interelectronic repulsion within the t_{2g} set of orbitals or the e_g set or both sets in the Fe(II) ion. It is well known that the effect of π and σ bonding in d^6 complexes cannot be distinguished by the use of these spectral data.[16] However, the complexes of Cr(III) can be utilized to obtain direct information about the interelectronic repulsions within the t_{2g} subshell.

The d^3 Complexes.—The first electronic transition which has been observed for *trans*-[$CrCl_2(das)_2$][ClO_4] is a weak shoulder at 13.3 kK. From the intensity and position of this band, it is assigned to the spin-forbidden transition $^4B_1 \rightarrow {}^2A_1$, $^2B_1$. The position of this transition is well within the range of energies usually found in other octahedral and tetragonal Cr(III) complexes.[17] The band of moderate intensity at 17.0 kK (Figure 3) is the lowest energy spin-allowed transition and must be assigned to the transition, $^4B_1 \rightarrow {}^4E$. The shoulder at 20.8 kK on the low-energy side of the main band at 23.6 kK is assigned to the transition $^4B_1 \rightarrow {}^4B_2$, while the two remaining transitions at 23.6 and 25.5 kK are from the $^4B_1$ ground state to the $^4B_1$ and ^4E components of the $^4T_1$, respectively.

Since the only chromium(III) *o*-phenylenebis(dimethylarsine) complexes available are $CrX_2(das)_2^+$, it is necessary to obtain the expressions for the energies of a d^3 ion in a tetragonal field. Detailed calculations have been made for tetragonal d^3 complexes[18] including the effects of configuration interaction. The expressions for the energy levels of a d^3 ion considering only the effects of a tetragonal field are shown in Figure 4, along with those for an octahedral complex. It can be seen that to a first approximation, the energy separation of the $^2T_1$, ^2E levels from the ground state in the tetragonal complex is the same as in the octahedral complex. It should also be noted that the $^4T_2$ level in the octahedral complex has the same energy as the $^4B_2$ component in the tetragonal complex. The splitting of the $^4T_2$ is a direct measure of *Dt*, while *Ds* can be evaluated from the splitting of the $^4T_1$. The values of these parameters for these chromium complexes are listed in Table IV.

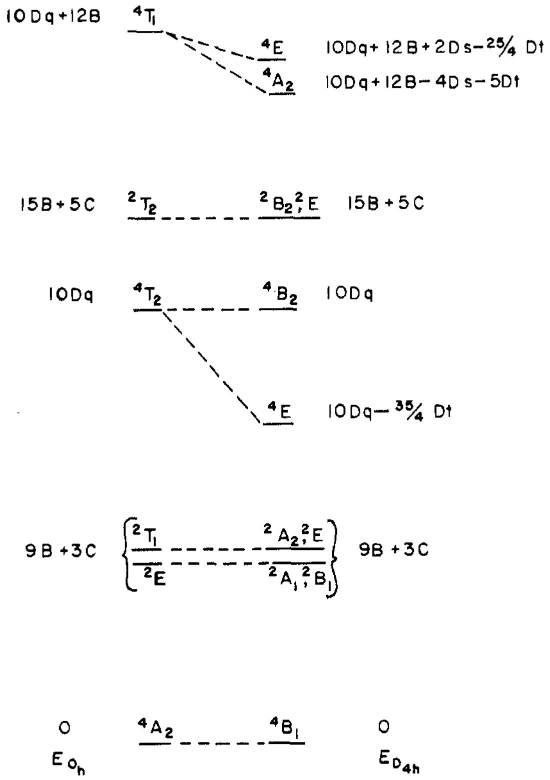

Figure 4.—The energy level expressions for a d^3 ion in an octahedral and tetragonal field.

In octahedral Cr(III) complexes, the first two excited states, $^2T_1$ and ^2E, which are almost degenerate, arise from the same electron configuration as the ground state, $^4A_2$ (t_{2g}^3). Thus, the energy separation between the $^4A_2$ ground state and the $^2T_1$ excited states can be taken as a measure of the interelectronic repulsions within the t_{2g} subshell. For a large number of chromium complexes, the $^2T_1$, ^2E level is known quite accurately.[17] The smallest energy separations between the $^2T_1$, ^2E level and the $^4A_2$ ground state and, consequently, the smallest interelectronic repulsions in the

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(15) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962, p 74.

(16) C. K. Jørgensen, *Progr. Inorg. Chem.*, **4,** 73 (1962).

(17) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20,** 1603 (1964).

(18) J. R. Perumareddi, *J. Phys. Chem.*, **71,** 3155 (1967).

TABLE IV

THE NEPHELAUXETIC RATIOS, β, AND LIGAND FIELD PARAMETERS FOR Cr(III) COMPLEXES

Complex	$10Dq^a$	$B_{55}{}^b$	Ds^b	Dt^b	β_{55}	β_{35}	β_{33}
$CrCl_2(das)_2{}^+$	20.8	633	407	435	0.69	0.60	0.52
$CrCl_2(en)_2{}^+$	22.0	690	378	537	0.75	0.68	0.60
$Cr(en)_3{}^{3+}$	21.9	715	...	...	0.77	0.60	0.47
$Cr(CN)_6{}^{3-}$	26.7	596	...	...	0.65	0.50	0.38

[a] In kK. [b] In cm^{-1}.

t_{2g} orbitals are obtained in those complexes containing π-bonding ligands. For example, the smallest energy separation is found with ligands such as cyanide in which the t_{2g} orbitals of Cr(III) π bond with the π orbitals of the cyanide. The resultant delocalization of the t_{2g} electrons reduces the interelectronic repulsion of the t_{2g} electrons. The largest energy separations between the $^2T_1$, ^2E level and the $^4A_2$ ground state are obtained with ligands such as ethylenediamine which cannot form π bonds with the t_{2g} orbitals of the metal. In these complexes the interelectronic repulsions will therefore be higher than in the case of π bonding ligands. The ratio B/B (free ion) or β is a convenient measure of the interelectronic repulsions within a shell or subshell.[16] Since it is impossible to determine both B_{55} and C simultaneously from the single transition $^4A_2 \rightarrow {}^2T_1$, ^2E, it was assumed that $C = 4B_{55}$. Thus, the energy separation between the ground term and the $^2T_1$, ^2E terms is approximately $21B_{55}$.

The terms $^4T_1$ and $^4T_2$ arise from the electron configuration $t_{2g}{}^2e_g$ in which an electron has been promoted from the t_{2g} orbitals into the e_g orbitals. In an octahedral complex, these two terms are separated by $12B_{35}$, where now B_{35} is determined by the interelectronic repulsion between the t_{2g} and e_g orbitals. Using spectral data for the chromium compounds from Table IV and the values of Ds and Dt determined above, it is possible to calculate the positions of the $^4T_1$ and $^4T_2$ and thereby B_{35}. Similar calculations have also been carried out for the ethylenediamine complexes using the data from the literature[15] (Table IV). These calculations show that such a procedure gives essentially the same values of β_{55} for the tetragonal and octahedral ethylenediamine complexes and therefore is a satisfactory method for obtaining β_{55} for the *o*-phenylenebis(dimethylarsine) complexes. β_{33} can be calculated[16] from the values of β_{55} and β_{35} by use of the relationship $\beta_{35}{}^2 = \beta_{33}\beta_{55}$.

One of the most striking features of these results is the close relationship between the ethylenediamine and *o*-phenylenebis(dimethylarsine) complexes. β_{33}, β_{35}, and β_{55} for $CrCl_2(das)_2{}^+$ are all somewhat reduced from the values in the corresponding ethylenediamine complexes. This can be easily understood in terms of central field covalency. The σ electrons which are utilized by the arsenic for binding with Cr(III) are more diffuse and more polarizable than the σ electrons on ethylenediamine, with the result that the effective nuclear charge on Cr(III) in $CrCl_2(das)_2{}^+$ is somewhat less than that on the chromium in $CrCl_2(en)_2{}^+$. This lower charge on the chromium in $CrCl_2(das)_2{}^+$ should affect the t_{2g} and e_g electrons equally and result in both β_{33} and β_{55} being smaller than in the ethylenediamine complex. If $d\pi$–$d\pi$ bonding were important in $CrCl_2(das)_2{}^+$, β_{55} should be greatly reduced compared with β_{33}. It is encouraging to note that the values of β_{55} for $Cr(en)_3{}^{3+}$ and $CrCl_2(en)_2{}^+$ are essentially identical. This is to be expected since neither ethylenediamine nor chloride is a good π-bonding ligand. The difference between β_{33} for $Cr(en)_3{}^{3+}$ and β_{33} for $CrCl_2(en)_2{}^+$ is expected since β_{33} is a measure of the interelectronic repulsion within the e_g orbitals. Moreover, since ethylenediamine forms better σ bonds than does the chloride ion, β_{33} for $Cr(en)_3{}^{3+}$ should be less than β_{33} for $CrCl_2(en)_2{}^+$ as is found to be the case (Table IV).

In $Cr(CN)_6{}^{3-}$, in which π bonding between the chromium and cyanide ligands is important, β_{55} is smaller than in any other compound thus far investigated except tris(dithiophosphato)chromium(III). Compared with ethylenediamine, these data indicate that the empty $d\pi$ orbitals on the arsenic do not participate in π bonding with the t_{2g} orbitals on the chromium. The reasons for this are readily apparent. First, Cr(III) would have a +3 charge, which is to some extent reduced by the central field covalency. However, the charge is probably still between +1 and +2 so that, in order to preserve electroneutrality, the chromium would need to acquire more electrons rather than increase its positive charge by "back π bonding" with the arsenic ligand.

Jørgensen[16] has shown that both the metal and the ligand contribute to β_{35}: $1 - \beta_{35} = h(\text{ligand})k(\text{central ion})$. He has evaluated both h and k for a number of metal ions and ligands. Using the values in Table IV for β_{35} and Jørgensen's value of 0.21 for k(chromium), h(*o*-phenylenebis(dimethylarsine)) is found to be 1.9 which should be compared with values of 2.0 for Cl^- and 2.3 for Br^-. From this value of h and for k(cobalt) = 0.35, β_{35} for $Co(das)_3{}^{3+}$ is calculated to be 0.33 compared with that found for $Fe(das)_3{}^{2+}$ of 0.36. These values are internally consistent, again indicating that there are no special effects of π bonding between the metal and *o*-phenylenebis(dimethylarsine).

All of the compounds included in this investigation contain metal ions with initial high positive charges (+2 and +3). "Back π bonding" will tend to increase the positive charge on the metal, so that in these complexes this type of π bonding would be unfavorable. These conclusions should not be generalized to include compounds such as $Cr(CO)_2(das)_2$ in which the metal has a lower oxidation number. In these compounds, $d\pi$–$d\pi$ bonding may become more important owing to the decreased positive charge on the central metal.

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