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THE ROLE OF ELECTRONIC SPECTRA IN THE STEREOCHEMISTRY OF COORDINATION COMPOUNDS

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CONTENTS

ABBREVIATIONS

das,	*o,o'*-phenylenebis(dimethylarsine), abbreviated also as diarsine
dip,	α,α'-dipyridyl
en,	ethylenediamine
naphal,	5:6-benzosalicylideneiminate
Ph,	phenyl (C_6H_5)
X–Ph,	monosubstituted phenyl ($X \cdot C_6H_4$)
py,	pyridine
sal · R,	*N*-substituted salicylideneiminate
3-CH_3O · sal · R,	*N*-substituted 3-methoxysalicylideneiminate
tas,	methylbis(3-propyldimethylarsine)

A. INTRODUCTION

One of the most fundamental aims in understanding the electronic spectra of transition metal complexes is their complete and unambiguous assignment in terms of the energy level scheme and chemical bonding. To do this completely is often a troublesome and painstaking task.

Once the assignment is established with certainty for complexes of a group, it is then possible to make use of this as a criterion or a basis for the consideration of other problems related with this in one way or another. There are some cases where the spectral pattern for a d^n system is well characterized, although the complete assignment of the absorption bands is not settled. In this case, the electronic spectrum may be used for diagnostic purposes. From this point of view, the extensively studied and well established systems are d^3, d^6 (low-spin), d^7, d^8 and d^9 systems. Other systems (d^1, d^2, d^4 and d^5 systems) are not as well understood, but as fundamental studies are being carried out to accumulate more data, correlation of the spectral pattern with the configuration of the metal complex has a firmer foundation. The d^3, d^6 and d^7 systems are considered in this article. In connection with more recent developments in this area, the results of the research carried out at our Laboratory will be presented.

There are many compounds in which a cooperative effect is present[1,2]. These compounds, which include those with an interaction, direct or indirect, between metal ions, are also interesting in many respects, but will not be discussed in this article.

B. d^3 AND d^6 SYSTEMS

(i) *Polarized crystal absorption spectra*

Polarized crystal spectra are useful for many purposes[1,2]. In addition to their application to the study of various problems in inorganic chemistry, they are useful for the assignment of absorption bands of compounds. As great improvements have been made in instruments in recent years, the measurements of the polarized crystal spectra is becoming more and more accurate and convenient. In fact, many papers, mainly concerned with band assignment, have appeared recently. In the present article, however, no attempt will be made to review all the recent results in this field. We will be concerned mainly with the application of the

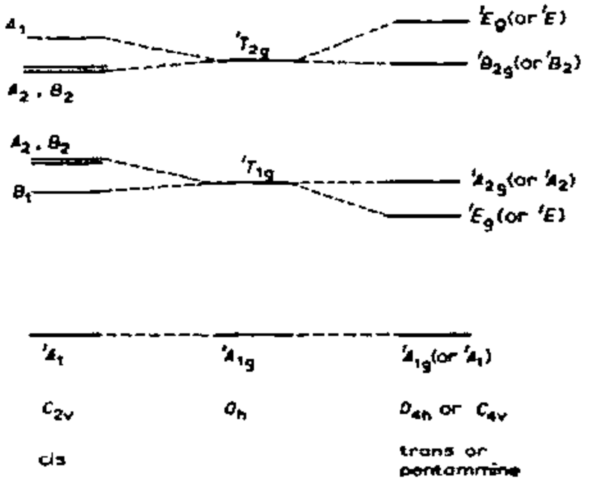


Fig. 1. Splittings of ligand field bands of six-coordinated complexes of cobalt(III) under lower field symmetries.

polarized crystal spectra to estimating the band splittings of typical coordination compounds.

For d^3 and d^6 systems, such as six coordinate chromium(III) and cobalt(III) complexes, the electronic spectra have been extensively studied, and correlation between the spectrum and the configuration of the metal complex has been established empirically and theoretically. In fact, the electronic spectrum has often been used for determining the configuration of metal complexes.

The ligand field bands of octahedral d^3 and d^6 complexes are expected to undergo splittings, when the symmetry of the complexes becomes lower, as shown in Fig. 1.

One of the classical examples showing the splitting of the ligand field bands is *trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$[3]. Since the crystal structure was known, the precise interpretation of the dichroism was possible[4]. Recently we have determined the polarized crystal spectra of *trans*-$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ at 290 °K[5]; the crystal structure of this complex is similar to the corresponding cobalt(III) complex (Fig. 2)[5]. The ligand field band at about $17.3 \cdot 10^3 cm^{-1}$ is strongly polarized along the *z*-axis of the complex, and the band at about $22.1 \cdot 10^3$ cm^{-1} is polarized along the $Cr(en)_2$-plane. Mainly on the basis of these polarization data, these absorption bands are assigned as shown in Table I, where the data with *cis*-$[Cr(en)_2Cl_2]Cl$ are also given. It seems to be particularly significant that the splitting of Band II is definitely observed. The details of the work will be reported elsewhere shortly.

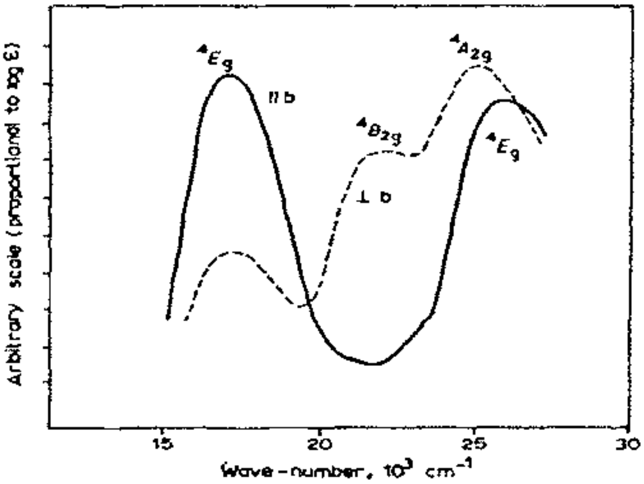


Fig. 2. Dichroism of *trans*-$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ on (100) face at 290 °K. The full line shows the spectrum with light having electric vector parallel to the Cl–Cr–Cl axis, and the dashed line shows the spectrum with light having electric vector perpendicular to the Cl–Cr–Cl axis.

When the crystal structure of the compound is not known, it is not possible to make such a precise analysis of the crystal spectrum. There are, however, some

TABLE 1

ABSORPTION MAXIMA (in kK) OF *trans*-$[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ AND *cis*-$[Cr(en)_2Cl_2]Cl$ DETERMINED FROM THE POLARIZED CRYSTAL SPECTRA

	Band I		*Band II*	
	a	*b*	*a*	*b*
trans-$[Cr(en)_2Cl_2]^+$	17.3	22.1	25.3	26.5
polariz.	z	xy	xy	z
assign.[a]	${}^4E_g$	${}^4B_{2g}$	${}^4A_{2g}$	${}^4E_g$
cis-$[Cr(en)_2Cl_2]^+$	18.1	19.4	24.5	25.2
polariz.	xy	z	z	xy
assign.[b]	${}^4A_1$	${}^4A_2$, ${}^4B_2$	${}^4A_2$, ${}^4B_2$	${}^4B_1$

[a] From the ground state ${}^4B_{1g}$. [b] From the ground state ${}^4B_1$.

cases where the arrangement of the complexes in the crystal may be inferred from the crystal spectra, so that the polarization of the absorption bands may be determined qualitatively. Above all, the positions of the split components can be determined accurately from the polarized crystal spectrum.

The band splittings of ligand field bands of chromium(III) and cobalt(III) complexes were thoroughly treated from a theoretical point of view, and a molecular orbital approach was developed in terms of σ and π empirical parameters[6, 7]. An attempt was recently presented to interpret the band splittings on the basis of the crystal field model[8].

In order to estimate the magnitude of the band splittings, the solution spectra have often been used[8, 9]. In many cases, however, it is difficult to estimate the band splittings from the solution spectra with reasonable accuracy and without too much arbitrariness. The band splittings, which were obtained through a rather artificial analysis of the absorption bands of the solution spectra, often suffered from errors arising from the arbitrariness involved in the method. Some of the splittings derived in this way may not be of any significance. It seems to be evident that the polarized crystal spectra may be used more successfully for the determination of the band splittings, since the split components are often observed in the polarized crystal spectra as separated peaks with different polarization properties. The complexes in the crystal are actually under the perturbing effect of the surrounding ions, but it is assumed to the first approximation that the crystal spectrum represents the spectrum of the complex itself.

Polarized crystal spectra have been determined at room temperature with the following compounds[10].

(a) pentammine series: $[Co(NH_3)_5Cl](ClO_4)_2$, $[Co(NH_3)_5Br]Br_2$, $[Co(NH_3)_5OH_2]_2(SO_4)_3$ and $[Co(NH_3)_5NCS](NCS)_2$

(b) *trans*-complexes: $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$, $[Co(en)_2Cl_2]ClO_4$, $[Co(en)_2Br_2]Br \cdot HBr \cdot 2H_2O$, $[Co(en)_2(OH_2)_2]Cl_3 \cdot 2H_2O$, $[Co(en)_2(NO_3)_2]NO_3 \cdot HNO_3 \cdot H_2O$, $[Co(en)_2(NH_3)_2]Cl_3 \cdot H_2O$, $[Co(en)_2(NCS)_2]Cl \cdot H_2O$,

$[Co(en)_2(NO_2)_2]NO_3$, $Na[Co(en)_2(SO_3)_2]$ and $[Cr(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$
(c) *cis*-complexes: $[Co(en)_2Cl_2]Cl$, $[Co(en)_2Br_2]Br$, $[Co(en)_2(OH_2)_2]Cl_3$ and $[Cr(en)_2Cl_2]Cl$.

The assignment of ligand field bands may be made in a similar scheme as previously given. In deriving the maximum frequency of the split component, the possibility that the other component might contribute some of the intensity is considered. The band maxima of the split components, together with proposed assignments, are given in Tables 2 and 3. There are several points of particular interest, which will be briefly discussed below.

TABLE 2

ABSORPTION MAXIMA (in kK) OF LIGAND FIELD BANDS OF COBALT(III) COMPLEXES DETERMINED FROM THE POLARIZED CRYSTAL SPECTRA

	Band I		*Band II*	
X	*a*	*b*	*a*	*b*
$[Co^{III}(NH_3)_5X]$				
NCS^-	20.7	21.5	—	—
OH_2	19.7	20.9	sh	sh
Cl^-	18.3	20.3	27.1	28.3
Br^-	17.8	20.1	—	—

Band Ia, $^1E \leftarrow {}^1A_1$ (polarized along z); Ib, $^1A_2 \leftarrow {}^1A_1$ (along xy); Band IIa, $^1B_2 \leftarrow {}^1A_1$ (along xy); IIb, $^1E \leftarrow {}^1A_1$ (along z); sh, shoulder.

trans-$[Co(en)_2X_2]$				
NO_2^-	23.0	(22)	29.0	—
NCS^-	19.9	21.8	—	—
NO_3^-	18.7	23.6	27.9	28.7
OH_2	18.6	21.3	28.1	29.6
SO_3^{2-}	17.5	20.0	—	—
Cl^-	16.0	22.7	—	—
Br^-	14.9	21.7	—	—

Band Ia, $^1E_g \leftarrow {}^1A_{1g}$ (along z); Ib, $^1A_{2g} \leftarrow {}^1A_{1g}$ (along xy); Band IIa, $^1B_{2g} \leftarrow {}^1A_{1g}$ (along xy) IIb, $^1E_g \leftarrow {}^1A_{1g}$ (along z).
The observed polarization property is shown in parenthesis.

TABLE 3

ABSORPTION MAXIMA (in kK) OF LIGAND FIELD BANDS OF *cis*-$[Co(en)_2X_2]$ DETERMINED FROM THE POLARIZED CRYSTAL SPECTRA

	Band I		*Band II*	
X	*a*	*b*	*a*	*b*
OH_2	19.7	20.9	sh	sh
Cl^-	17.3	19.3	24.8	25.6
Br^-	17.3	19.7	23.9	—

Band Ia, $^1B_1 \leftarrow {}^1A_1$ (along xy); Ib, $^1A_2, {}^1B_2 \leftarrow {}^1A_1$ (along z); Band IIa, $^1A_2, {}^1B_1 \leftarrow {}^1A_1$ (along z); IIb, $^1A_2 \leftarrow {}^1A_1$ (along xy).

It is to be noted that the splitting of band II is definitely observed for such complexes as *trans*-$[Cr(en)_2Cl_2]^+$ and *cis*-$[Cr(en)_2Cl_2]^+$. Band II, which is due to the $^1T_{2g} \leftarrow {}^1A_{1g}$ and $^4T_{1g} \leftarrow {}^4A_{2g}$ transition of the cobalt(III) and chromium(III) complexes, respectively, (with O_h symmetry), is expected to undergo the splitting as the symmetry becomes lower, but no unambiguous splitting has so far been observed in the solution spectra. In particular, both *cis*- and *trans*-forms of $[Cr(en)_2Cl_2]^+$ show the split components of Band II very clearly. The splittings of both Band I and Band II are also observed for *trans*-$[Co(en)_2X_2]$ ($X = OH_2$, NO_3^-), $[Co(NH_3)_5X]$ ($X = OH_2$, Cl^-) and *cis*-$[Co(en)_2X_2]$ ($X = OH_2$, Cl^-).

For $[Co(NH_3)_5NCS]^{2+}$ and *trans*-$[Co(en)_2(NCS)_2]^+$, it was claimed that the complexes showed no splitting for Band I, assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition of the complex with O_h symmetry. No splitting can be detected in the solution spectrum. The splitting, however, is clearly observed in the crystal spectrum, the polarization of one split component being the reverse of the polarization of the other. The extremely low intensity of the (en)–Co–(en) band ($21.8 \cdot 10^3\ cm^{-1}$) as compared with the SCN–Co–NCS band ($19.9 \cdot 10^3\ cm^{-1}$) may be related with the high position of NCS^- in the hyperchromic series[11].

The same situation arises for *trans*-$[Co(en)_2(SO_3)_2]^-$, where a quite similar pattern is observed. In this case, the split component Ia is much weaker (at least several times) than Band Ib. For all these complexes, the ligands or one of them along z-axis are those which stand high in the hyperchromic series.

In a similar way, one of the split components of Band I is much more intense than the other component for *trans*-$[Co(en)_2(NO_2)_2]^+$, where NO_2^- is also much higher than en in the hyperchromic series.

In many cases, the magnitude of the band splitting seems to parallel the separation of the ligands, along the z-axis and the xy-plane, in the spectrochemical series. This, however, may not be the case, when the contribution of π-bonding becomes significantly large in the metal–ligand linkage. As an example may be cited a series of nitro-complexes. The complex, *trans*-$[Co(en)_2(NO_2)_2]^+$, shows two split components for Band I, one being far more intense than the other, but the frequencies of these two split components are very close to each other. According to Schaffer and Jørgensen[12], the magnitude of the splitting of *trans*-dinitro-complexes is given by the expression (1). The second term in (1) is much larger than

$$\tfrac{3}{2}e'_{\sigma NH_3} - \tfrac{3}{2}e'_{\sigma NO_2} + 2e'_{\pi NO_2} \qquad (1)$$

the first term, and the total sum will not be a large value, since the third term contributes a positive value.

It has been concluded from experiments[13] and theories[6, 7] that the band splittings of the pentammine series are about the same as those of the *cis*-complexes, and that the band splittings of the *trans*-complexes are nearly twice as those of the *cis*- and the pentammine series. The present work confirms this approximation. Closer inspection of the experimental data reveals, however, that the band splittings of the *cis*-series are almost equal to those of the pentammine series, but that the band splittings for the *trans*-series are always slightly larger than twice the splittings of the *cis*-series. The reason for this fact is not quite clear for the moment; it may be due partly to the contribution of the cross term in the energy matrix, or may indicate the importance of the specific effect of the ligands in the *trans*-positions.

The values of dσ and dπ, which have been calculated according to the theory of Yamatera and McClure, are shown in Table 4. As mentioned above, the values of dσ and dπ derived for *cis*-$[Cr(en)_2Cl_2]^+$ are greatly different from those derived for the *trans*-series.

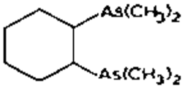
TABLE 4

THE VALUES OF dσ AND dπ (in kK) FOR COBALT(III) AND CHROMIUM(III) COMPLEXES

X	dσ	dπ	*Source of data*
Co(III) complexes			
Cl^-	−1.60	0.40	pentammine-series
Cl^-	−1.60	0.40	*cis*-series
OH_2	−0.85	0.50	*trans*-series
NO_2^-	−1.42	1.00	*trans*-series
Cr(III) complexes			
Cl^-	−1.00	0.20	*cis*-series
Cl^-	−1.50	0.90	*trans*-series

(*ii*) *Spectra of metal diarsine complexes*

In addition to ligand field bands, "specific absorption bands", due to charge transfer mechanisms (CT bands) and to internal transitions within ligands, may sometimes appear at comparatively low frequencies. The "specific absorption bands", due mainly to charge transfer between the metal ion and the halide ion, have long been known, but some other ligands also give rise to specific bands in the low frequency region. These ligands include, for example, phosphorus-, arsenic- and sulphur-containing ligands, which are unusual in many respects, perhaps because of the π-bonding between these ligands and the metal ion. In this connection, we will be concerned here with metal complexes of arsenic-containing ligands, in particular diarsine(I)[14].



(I)

For $[Co(das)_3]^{3+}$, two spin-allowed ligand field bands are expected to appear, corresponding to the transitions $^1T_{1g} \leftarrow {}^1A_{1g}$ and $^1T_{2g} \leftarrow {}^1A_{1g}$. One of these two ligand field bands is observed as a separate peak in the lower frequency region, but the other is hidden by stronger absorption bands, due to charge transfer and internal transitions within the ligands, as shown in Fig. 3. The strong absorption band at about $25.9 \cdot 10^3$ cm^{-1} is considered to be due to the charge transfer mechanism: $Co^{III}(d^*) \leftarrow As(\sigma)$.

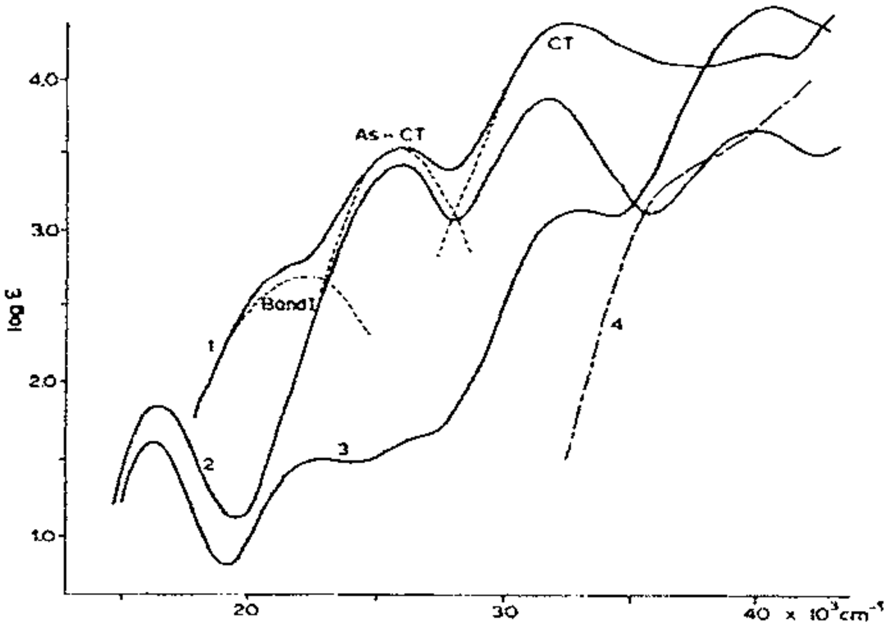


Fig. 3. Absorption spectra of cobalt(III) complexes in solution. (1) $[Co(das)_3](ClO_4)_3$ in 50% ethanol; (2) *trans*-$[Co(das)_2Cl_2]ClO_4$ in ethanol; (3) *trans*-$[Co(en)_2Cl_2]ClO_4$ in water; (4) diarsine in ethanol.

Since Band II ($^1T_{2g} \leftarrow {}^1A_{1g}$) is hidden by the charge transfer band, it is not possible to obtain the exact value of *Dq* for this complex. It is possible, however, to estimate an approximate *Dq* value and determine the position of das in the spectrochemical series from the maximum frequency of Band I ($^1T_{1g} \leftarrow {}^1A_{1g}$): (das) > (en) > NH_3. The optical electronegativity[15] for diarsine is estimated approximately to be 2.46, lower than iodide as well as chloride and bromide.

It is to be noted that the intensity of the ligand field band I of $[Co(das)_3]^{3+}$ is much higher than that of the corresponding bands of the ammine complexes, as shown in Table 5. This is probably due to the mixing in of the strong CT bands on the ligands, and the mixing of the d- and p-orbital function on the metal.

Electronic absorption spectra were also determined with complexes of the $[Co^{III}(das)_2X_2]$-type, for which two isomers corresponding to *cis*- and *trans*-

TABLE 5

ABSORPTION MAXIMA OF LIGAND FIELD BAND I ($^1T_{1g} \leftarrow {}^1A_{1g}$) OF [$Co^{III}A_6$] OR [$Co^{III}B_3$]

A or B	*ν, kK*	*log ε*
CN^-	32.3	2.29
(das)	22.2	2.70
(dip)	22.2	1.84
(en)	21.3	1.94
NH_3	21.0	1.68
H_2O	16.3	1.60

configurations are possible. It proved to be possible to determine the configurations of the isomers of $[Co(das)_2Cl_2]^+$ and $[Co(das)_2Br_2]^+$ from their electronic spectra. The two isomers of these were prepared as crystals, one being green, and the other, violet. The green isomers of $[Co(das)_2Cl_2]^+$ and $[Co(das)_2Br_2]^+$ show an absorption band at about 16.4 and $15.7 \cdot 10^3$ cm^{-1}, respectively. The band maxima lie at lower frequencies, when compared with the corresponding ethylenediamine complexes with a *cis*-configuration (18.6 and $18.1 \cdot 10^3$ cm^{-1}, respectively). Since (das) stands higher than (en) in the spectrochemical series, the comparison of the band maxima clearly shows that the green isomers have a *trans*-configuration. A *cis*-configuration is assigned to the violet forms of $[Co(das)_2Cl_2]^+$ and $[Co(das)_2Br_2]^+$.

For $Co(das)_2I_3$, only one of the two isomers is known, and this is usually obtained as dark-purple crystals. The compound shows a ligand field band Ia at a much higher frequency ($18.5 \cdot 10^3$ cm^{-1}) than the *trans*-$[Co(das)_2Cl_2]^+$ and $[Co(das)_2Br_2]^+$. It is concluded, therefore, that the dark-purple complex $Co(das)_2I_3$ does not have a *trans*-configuration, but has two iodide in *cis*-positions.

It seems to be empirically believed that most of the bis(diarsine)metal complexes with six-coordination have a *trans*-configuration, when only one of the two isomers is known. This has been well substantiated so far, but the iodocobalt(III) complex discussed above is an exception to this.

It is interesting that $[Co(das)_2(CNS)_2]^+$ shows a ligand field band Ia at a considerably lower frequency ($18.8 \cdot 10^3$ cm^{-1}), when compared with the corresponding ethylenediamine complexes ($19.8 \cdot 10^3$ and $19.7 \cdot 10^3$ cm^{-1} for the *cis*- and the *trans*-bis(ethylenediamine) complex, respectively). The electronic spectrum alone seems to indicate that the sulphur atom of the thiocyanate group may perhaps be coordinated to the cobalt(III) ion. The infrared spectrum of the complex, however, favours the Co–N bond, according to the current criterion[16]. This discrepancy cannot be explained at the moment.

Examination of the band maxima (Tables 5 and 6) yields the following order for the spectrochemical series: NO_2^- > (das) > (dip) > (en) > NH_3. It is again seen that the band intensity of the diarsine complexes is considerably higher than that of the corresponding ammine complexes. In particular, the complexes with a *cis*-configuration exhibit ligand field bands with a higher intensity.

TABLE 6

THE LOWER COMPONENT OF BAND I (BAND IA) FOR *trans*-$[Co^{III}B_2X_2]^+$ (ν, in kK)

X	*B* = (*das*)		*B* = (*en*)	
	ν	*(log ε)*	ν	*(log ε)*
NO_2^-	23.5	(3.00)	23.3	(2.20)
CNS^-	18.8	(2.58)	19.7	(2.42)[b]
CH_3COO^-	18.7	(1.88)	18.6	(1.73)
Cl^-	16.4	(1.85)	16.1	(1.61)
Br^-	15.7	(1.94)	15.2	(1.73)

[a] The data for the ethylenediamine complexes are taken from ref. 13 and M. LINHARD AND M. WEIGEL, *Z. Anorg. Allgem. Chem.*, 264 (1951) 324.

[b] The nitrogen atom of the CNS^- is bound with the cobalt(III) ion in the bis(ethylenediamine) complex.

All these diarsine complexes of cobalt(III) show As–CT bands in the comparatively low frequency region, and the absorption curves are thereby made much more complicated in appearance than the curves of the corresponding ammine complexes.

For $[Rh(das)_2Cl_2]^+$, $[Rh(das)_2Br_2]^+$ and $[Ir(das)_2Cl_2]^+$, only one of the two geometrical isomers has so far been obtained[17]. From the low frequency and the low intensity of the ligand field band Ia, when compared with the corresponding amine compounds, it is concluded that they all have a *trans*-configuration, as shown in Table 7.

TABLE 7

ABSORPTION MAXIMA (in kK) OF $[M^{III}A_4Cl_2]^+$

A	*M* = *Co(III)*		*M* = *Rh(III)*		*M* = *Ir(III)*	
(das)	16.4	1.85	24.7	2.27	29.1	2.10
(en)	16.1	1.62	24.6[a]	1.88	28.9	1.66[b]
(py)[c]	15.8	1.64	24.3	1.85	no data	

[a] Taken from S. ANDERSON AND F. BASOLO, *J. Am. Chem. Soc.*, 82 (1960) 4423.

[b] Taken from S. KIDA, *Bull. Chem. Soc. Japan*, 39 (1966) 2415.

[c] Taken from A. v. KISS AND D. v. CZEGLEDY, *Z. Anorg. Allgem. Chem.*, 235 (1938) 407.

It is found that the spin-forbidden band of $[Ir(das)_2Cl_2]^+$ at about $24.9 \cdot 10^3$ cm^{-1} bas a considerably high intensity (log ε 1.40). For these diarsine complexes, too, the intensity of ligand field bands is found to be higher than the intensity of the corresponding ammine complexes.

The ratio of the frequency of the $^1E_g \leftarrow {}^1A_{1g}$ band maximum is 1:1.58:1. for Co^{III}:Rh^{III}:Ir^{III}. These values agree with the values for complexes of other typical ligands[15]. The As-CT bands and halide-CT bands are shifted toward higher frequencies in the order: $Co^{III} < Rh^{III} < Ir^{III}$. This is in agreement with the prediction based upon the "optical electronegativity" taking the ligand field splitting into account.

The diamagnetic $[Ni^{II}(das)_2](ClO_4)_2$ complex shows absorption bands which are typical of a planar nickel(II) complex, as shown in Fig. 4. Comparison of the ligand field band maximum with the band maxima of other square-planar complexes shows that diarsine stands very high in the spectrochemical series and in the hyperchromic series.

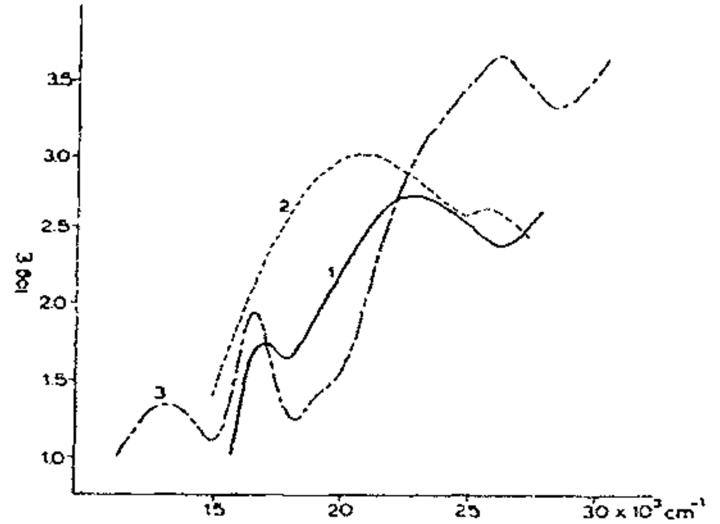
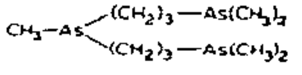


Fig. 4. Absorption spectra of diarsine nickel complexes in ethanol. (1) $[Ni^{II}(das)_2](ClO_4)_2$; (2) $[Ni^{II}(das)_2Cl]Cl$; (3) $[Ni^{III}(das)_2Cl_2]Cl$. The curve 2 is taken from C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, (1960) 4379.

The spectrum of $[Ni(tas)_2](ClO_4)_2$, which was reported previously[18], is found to be typical of a square-planar nickel(II) complex. The ligand (tas) usually



$$CH_3{-}As\begin{matrix}\diagup (CH_2)_3{-}As(CH_3)_2\\ \diagdown (CH_2)_3{-}As(CH_3)_2\end{matrix}$$

(II)

functions as a terdentate ligand, but this is bidentate in the above complex. The octahedral complex $[Ni(das)_3](ClO_4)_2$, which is diamagnetic, was studied thoroughly, and its electronic spectrum was interpreted on the basis of electrical asymmetry arising from σ- and π-bonding in a D_3 field[19]. It seems that the pattern of the absorption spectrum of the unusual $[Ni(das)_3]^{2+}$ ion is not so different from that of the planar $[Ni(das)_2]^{2+}$, except for the much higher intensity of the former, at least as far as ligand field bands are concerned.

The As-CT band does not appear in the frequency region lower than about $30 \cdot 10^3$ cm^{-1}, in these nickel(II) complexes (including the penta-coordinated complexes, $[Ni(das)_2X]^+$), in agreement with the comparatively high value of the "optical electronegativity" of nickel(II).

Some nickel(III) complexes are known with diarsine as a ligand. The electronic spectrum of $[Ni^{III}(das)_2Cl_2]^+$, which is of a low-spin type, is quite different from the spectra of the nickel(II) complexes. The nickel(III) complex shows three peaks at about $13.2 \cdot 10^3$, $16.6 \cdot 10^3$ and $19.2 \cdot 10^3$ cm^{-1}, which correspond to spin-forbidden d-d transitions. The corresponding bromonickel(III) complex shows a similar spectrum with the corresponding bands at slightly lower frequencies. For the chloronickel(III) complex, the strong absorption band at about $24 \cdot 10^3$ cm^{-1} may be assigned as an As-CT band, which is most probably due to a transition from As to nickel(III).

Diarsine complexes of many other metal ions exhibit complicated spectra with As-CT bands in the lower frequencies and with ligand field bands which are more intense than those of typical ammine complexes. There are those complexes which show ligand field bands with molar extinction coefficient of order of 10^3. These complexes include, for example, $[M^{III}(das)_2X_2]^+$ and $[Re^{II}(das)_2X_2]$, where M^{III} denotes Tc, Re and Os, and X denotes Cl and Br.

Several metal complexes with phosphorus-containing ligands are also known to show so-called "ligand field bands" with anomalously high intensity.

C. d^7 SYSTEM

For a d^7 system (Co^{2+}) or a d^8 system (Ni^{2+}), the electronic spectrum is well-defined for different configurations. The pattern of the electronic spectrum for the different configurations seems to be so characteristic that it is generally possible to use the electronic spectrum to determine the configuration of a complex. In fact, the electronic spectrum proved to be quite useful for determining the configurations of many complexes of the $[Co^{II}L_2X_2]$ and the $[Ni^{II}L_2X_2]$ type, which were concluded to take a tetrahedral or a planar configuration, depending upon the nature of L and X[20,21].

In the following discussion, we will consider only cobalt(II) complexes. The complexes of cobalt(II) are known to take a tetrahedral, an octahedral or a square-planar configuration. Taking Schiff bases of salicylaldehyde as ligands, the typical spectra for different configurations are shown in Fig. 5. The band assignment for the tetrahedral and the octahedral configuration may be made in a conventional way, as shown in the figure.

In addition to four- and six-coordination, five-coordination also appears for cobalt(II). The five-coordinated cobalt(II) compounds of a low-spin type have been known for some time[22], but the five-coordinated cobalt(II) compounds of a high-spin type have been characterized only recently. One of the first examples is afforded by $Co[sal \cdot 2,6\text{-}(CH_3)_2Ph]_2 \cdot py$, which is obtained from the pyridine

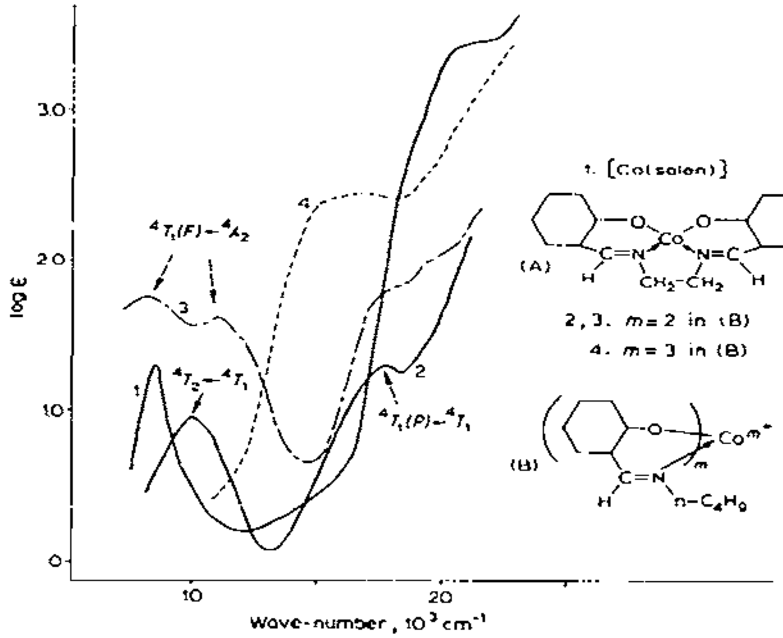
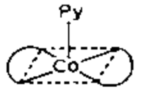
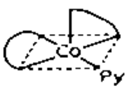


Fig. 5. Absorption spectra of Schiff base cobalt complexes in solution. (1) salicylaldehydebis-(ethylenediiminato)cobalt(II) in chloroform (planar); (2) $Co^{II}(sal \cdot n\text{-}C_4H_9)_2$ in pyridine (octahedral); (3) $Co^{II}(sal \cdot n\text{-}C_4H_9)_2$ in ethanol (tetrahedral); (4) $Co^{III}(sal \cdot n\text{-}C_4H_9)_3$ in ethanol (octahedral).

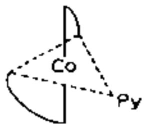
solution of the parent complex[23]. A possible configuration for this five-coordinated pyridine solvate may be one of the three configurations, (III), (IV) or (V). From examination of the steric condition, the structure (III) may be excluded. The structures (IV) and (V) are, in fact, rather similar.



(III)



(IV)



(V)

When the substituent (R) is Ph or X–Ph in $Co(sal \cdot R)_2$, the pyridine solvates obtained are always six-coordinate. Obviously the main factors favourable for the five-coordinated complex is the steric one in this case. On the contrary, for $3\text{-}CH_3O \cdot sal$, a similar procedure to the above yields not a five-coordinated solvate, but a different one with the formula, $Co(3\text{-}CH_3O \cdot sal \cdot 2{,}6\text{-}Y_2Ph)_2 \cdot (py)_2$, where Y denotes CH_3 or C_2H_5. From the electronic spectra, it is most likely that these pyridine solvates take a distorted octahedral configuration[24]. Electronic spectra of some of the penta-coordinated cobalt(II) complexes are shown in Fig. 6.

The difference between sal · R and $3\text{-}CH_3O \cdot sal$ is to be noted. The elec-

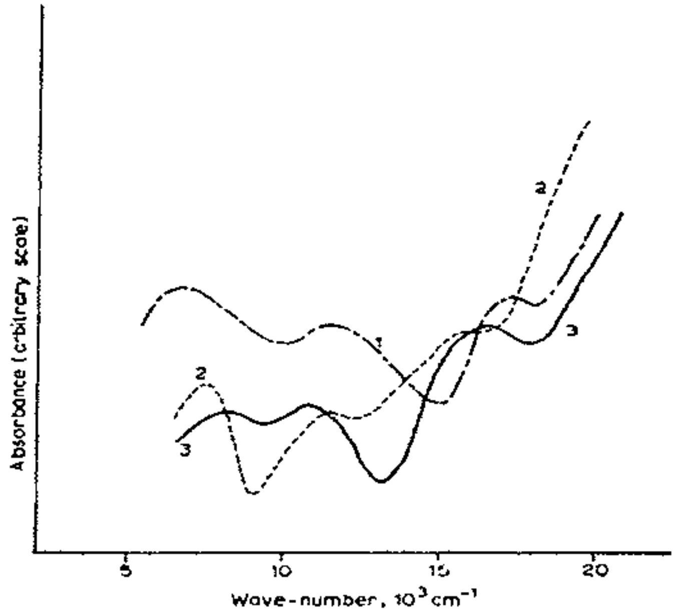


Fig. 6. Reflectance spectra of five-coordinated cobalt(II) complexes of a high-spin type. (1) Co[5-Cl · sal · $CH_2CH_2N(C_2H_5)_2]_2$; (2) Co[naphal · 2,6-$(CH_3)_2$Ph$]_2$ · py; (3) Co[sal · 2,6-$(CH_3)_2$Ph$]_2$ · py. The curve (1) is taken from L. SACCONI, M. CIAMPOLINI AND G. P. SPERONI, *Inorg. Chem.*, 4 (1965) 1116.

tronic factor seems to be important in this case. The ligand field seems to lie near the border in strength between the field favouring the five- and six-coordination, and a possibly small inductive effect by the 3-methoxy group may be strong enough to give rise to a different configuration.

Similar five-coordinated cobalt(II) complexes of a high-spin type have also been prepared[25]. These include Co(sal · 2,4,6-Br_3Ph$)_2$ · py and Co(naphal · R$)_2$ · py for R = 2,6-$(CH_3)_2$Ph and 2,6-$(C_2H_5)_2$Ph.

The configurations of Co_2(sal · $CH_3)_4$[26] and Co[5-Cl · sal · CH_2CH_2N-$(C_2H_5)_2]_2$[27] have been determined by X-ray structure analysis, the former being trigonal bipyramidal and the latter, square pyramidal.

Some other examples of five-coordinated cobalt(II) complexes of a high-spin type have also been recently reported[28,29]. A theoretical treatment of the electronic spectra of trigonal-bipyramidal cobalt(II) complexes of a high-spin type was presented. The agreement between this theory and experiments seems to be rather good particularly in view of the approximations in the theory. More detailed discussion of the electronic spectra should not be made until more data concerning the crystal structure and spectra of five-coordinated cobalt(II) complexes of a high-spin type are available.

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REFERENCES

1 S. Yamada in W. Schneider, G. Anderegg and R. Gut (Eds.), *Essays in Coordination Chemistry*, Birkhäuser, Basel, 1964, p. 140.
2 S. Yamada and R. Tsuchida, *Ann. Rep. Scient. Work, Fac. Sci. Osaka Univ.*, 4 (1956) 79.
3 S. Yamada, A. Nakahara, Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, 28 (1955) 222.
4 C. J. Ballhausen and W. Moffitt, *J. Inorg. Nucl. Chem.*, 3 (1956) 178.
5 S. Yamada, to be published.
6 H. Yamatera, *Bull. Chem. Soc. Japan*, 31 (1958) 95.
7 D. S. McClure in S. Kirschner (Ed.), *Advances in the Chemistry of Coordination Compounds*, McMillan, New York, 1961, p. 498.
8 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4 (1965) 709.
9 W. A. Baker, Jr. and M. G. Phillips, *Inorg. Chem.*, 5 (1966) 1042.
10 S. Yamada, *Proceedings International Symposium on Molecular Structure and Spectroscopy*, Science Council of Japan, Tokyo (1962) A403–1; also, unpublished work.
11 S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 26 (1953) 15.
12 C. E. Schäffer and C. K. Jørgensen, in press.
13 M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, 271 (1952) 101.
14 T. M. Dunn, R. S. Nyholm and S. Yamada, *J. Chem. Soc.*, (1962) 1564; also, unpublished work.
15 C. K. Jørgensen, in W. Schneider, G. Anderegg and R. Gut (Eds.), *Essays in Coordination Chemistry*, Birkhaüser, Basel, 1964, p. 98; *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, Oxford, 1962.
16 M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, 81 (1959) 6412; J. Lewis, R. S. Nyholm and P. W. Smith, *J. Chem. Soc.*, (1961) 4590; A. Turco and C. Pecile, *Nature*, 191 (1961) 66.
17 R. S. Nyholm, *J. Chem. Soc.*, (1950) 857.
18 R. V. Parish, Ph. D. Thesis, University College London (1958).
19 B. Bosnich, R. Bramley, R. S. Nyholm and M. L. Tobe, *J. Am. Chem. Soc.*, 88 (1966) 3926.
20 See, for example, T. Boschi, M. Nicolini and A. Turco in A. B. P. Lever (Ed.), *Coordin. Chem. Rev.*, 1 (1966) 133; F. A. Cotton, D. M. L. Goodgame and A. Sacco, *J. Am. Chem. Soc.*, 83 (1961) 4157; W. E. Hatfield and J. T. Yoke, *Inorg. Chem.*, 1 (1962) 475; N. S. Gill and R. S. Nyholm, *J. Inorg. Nucl. Chem.*, 18 (1961) 88; R. C. Stoufer, D. H. Busch and W. B. Hadley, *J. Am. Chem. Soc.*, 83 (1961) 3732; A. B. P. Lever and S. M. Nelson, *J. Chem. Soc.*, (1966) 859; A. Sacco and F. A. Cotton, *J. Am. Chem. Soc.*, 84 (1962) 2043.
21 See, for example, A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, (1963) 5042; L. M. Venanzi *et al.*, *J. Chem. Soc.*, (1961) 2705 and 4816; *ibid*, (1962) 693; G. Dyer and D. W. Meek, *Inorg. Chem.*, 4 (1965) 1398.
22 G. A. Barclay and R. S. Nyholm, *Chem. Ind. (London)*, (1953) 378; C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.*, (1960) 4379; G. A. Mair, H. M. Powell and L. M. Venanzi, *Proc. Chem. Soc.*, (1961) 170; R. G. Hayter, *Inorg. Chem.*, 2 (1963) 932; G. S. Benner, W. E. Hatfield and D. W. Meek, *Inorg. Chem.*, 4 (1965) 1544.
23 S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, 38 (1965) 683.
24 S. Yamada, *Coordin. Chem. Rev.*, 1 (1966) 415.
25 S. Yamada, E. Yoshida and Y. Kuge in W. Schneider (Ed.), *Proceedings Ninth International Conference on Coordination Chemistry*, Helv. Chim. Acta Verlag, Basel, 1966, p. 68; also, unpublished work.

26 P. L. Orioli, M. Di Vaira and L. Sacconi, *Chem. Commun. (London)*, (1965) 103.
27 L. Sacconi, P. L. Orioli and M. Di Vaira, *J. Am. Chem. Soc.*, 87 (1965) 2059.
28 M. Ciampolini, N. Nardi and G. P. Speroni, *Coordin. Chem. Rev.*, 1 (1966) 222.
29 Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, 88 (1966) 1394.
30 M. Ciampolini, *Inorg. Chem.*, 5 (1966) 35.