304. *The Spectra of Ditertiary Arsine Complexes. Part I. The Configuration of the Isomers of Dihalogenobisdiarsinecobalt*(III).

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Purple isomers of complexes [Co(diarsine)$_2$X$_2$]ClO$_4$ in which X = Cl or Br are described. The visible and ultraviolet spectra of these and of the previously reported green forms are discussed and it is concluded that the green form has the *trans-* and the purple form the *cis-*configuration.

MANY six-co-ordinate metal complexes of *o*-phenylenebisdimethylarsine (diarsine) have been described;[1] in no case, however, has geometrical isomerism been definitely established although it had been assumed to occur in the complexes of bivalent ruthenium[2] and bivalent osmium[3] of the type [M^{II}(diarsine)$_2$X$_2$]^0. Also, a study[4] of the carbonyl stretching frequency of the complex [Mo(diarsine)$_2$(CO)$_2$]^0 was interpreted as indicating a *cis-*arrangement of the carbonyl group.

This paper describes an investigation of some tervalent cobalt complexes in which an attempt was made to prepare the different isomers and to establish their configurations from visible and ultraviolet spectra. Such isomerism is well known for diacidotetrammino-complexes, the four nitrogen atoms being incorporated in four ammonia molecules or two ethylenediamine groups, etc.

It is well known[5,6] that cobalt(III) complexes have two absorption bands, with maximum molar extinction coefficients of about 100, in the visible and near-ultraviolet regions, and recent theoretical studies[7] suggest that for octahedral complexes having O_h point symmetry the two bands should be assigned as $^1T_{1g} \longleftarrow {}^1A_{1g}$ and $^1T_{2g} \longleftarrow {}^1A_{1g}$, the latter lying at the higher frequencies. It is convenient for the following discussion to refer to these ligand field bands as I and II, respectively.[8a] When the complex departs from O_h symmetry because of ligand inequality, these bands are split and for molecules of the type *trans-*[CoA$_4$X$_2$]$^{n\pm}$ with approximate D_{4h} symmetry, the ligand field band I yields two components[6,7] (Ia and b).

The *cis-*isomers of [CoA$_4$X$_2$]$^{n\pm}$ have only a C_{2v} point group symmetry and theory predicts[7b] that each of the ligand field bands will be split into three and that the overall splitting in band I will probably be only about half of that expected for the corresponding band of the *trans-*complex. Such conclusions had previously been reached from a study of the spectra alone.[9,10] It has also been shown, empirically,[10,11] that the shift of ligand field band Ia from the equivalent band of the hexammine complex always follows the same order, depending upon the acido-group, namely, ν_1(hexammine) $\gtrless \nu_1$(*cis-*diacido-complexes), $\gtrless \nu_{1a}$(*trans-*diacido-complexes). It is known that *trans-*dichlorobis(ethylenediamine)cobalt(III) has its lowest frequency band at about $16 \cdot 1 \times 10^3$ cm.$^{-1}$. This band has been identified as being part of the essentially ligand field band I of the perfect octahedral case, the *trans-*absorption being the low-frequency component of the split $^1T_{1g}$

[1] Nyholm and Sutton, *J.*, 1958, 560, and references therein.
[2] Nyholm and Sutton, *J.*, 1958, 567; Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153.
[3] Nyholm and Sutton, *J.*, 1958, 572.
[4] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803.
[5] Tsuchida, *J. Chem. Soc. Japan*, 1938, **59**, 536, 781, 819; von Kiss and Czegledy, *Z. anorg. Chem.*, 1938, **235**, 407; Linhard, *Z. Elektrochem.*, 1944, **50**, 224.
[6] Orgel, *J.*, 1952, 4756; Tanabe and Sugano, *J. Phys. Soc., Japan*, 1954, **9**, 753, 766; Yamatera, *Bull. Chem. Soc. Japan*, 1958.
[7] (a) Ballhausen and Moffitt, *J. Inorg. Nuclear Chem.*, 1956, **3**, 178; (b) Ballhausen and Jörgensen, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1955, **29**, No. 14; McClure, Proc. VIth Internat. Conference on Co-ordination Chemistry, Detroit, 1961, ed. Kirschner.
[8] Linhard and Weigel, *Z. anorg. Chem.*, 1953, **271**, 101.
[9] Basolo, *J. Amer. Chem. Soc.*, 1950, **72**, 4393; Ballhausen and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 810; Yamada, Nakahara, Shimura, and Tsuchida, *Bull. Chem. Soc. Japan*, 1955, **28**, 222.
[10] Linhard and Weigel, *Z. anorg. Chem.*, 1951, **267**, 121; Shimura, *Bull. Chem. Soc. Japan*, 1952, **25**, 49.
[11] Tsuchida, *Bull. Chem. Soc. Japan*, 1938, **13**, 388, 436.

state, *i.e.*, band Ia. The difference in the frequency of the first maximum makes it possible to decide between the assignments for the two isomers and, since the ligand " diarsine " is very close to (actually slightly higher than) ethylenediamine in the spectro-chemical series,[12] it seems likely that the stereochemistry of the diarsine complexes can be established by direct comparison. Thus the *trans*-[Co(diarsine)$_2$Cl$_2$]$^+$ ion should have its ligand field band Ia at a frequency a little higher than that of the corresponding ethylenediamine complex, but lower than that of the *cis*-isomer, while the *cis*-[Co(diarsine)$_2$Cl$_2$]$^+$ would also be expected to have its ligand field band I at a slightly higher frequency than the *cis*-ethylenediamine complex.
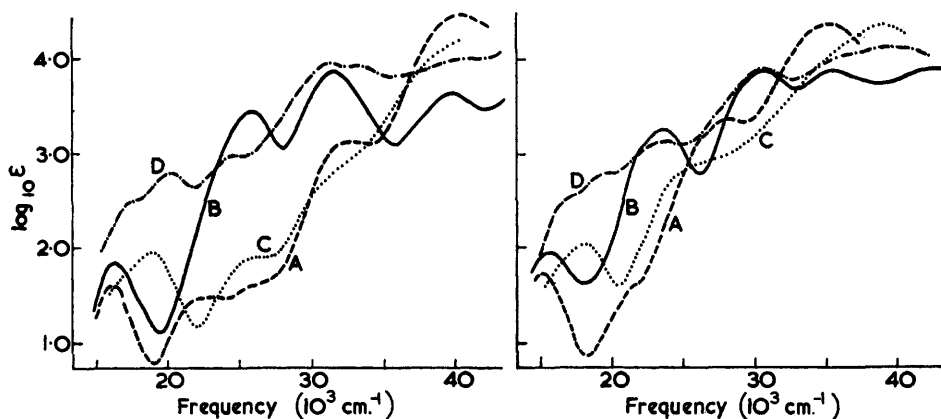

FIG. 1.　　　　　　　　　FIG. 2.

FIG. 1. Ultraviolet spectra of the complexes (A) *trans*-[Co enCl$_2$]ClO$_4$, (B) *trans*-[Co(diarsine)$_2$Cl$_2$]ClO$_4$, (C) *cis*-[Co en$_2$Cl$_2$]ClO$_4$, and *cis*-[Co(diarsine)$_2$Cl$_2$]ClO$_4$. A, C in H$_2$O; B, D in EtOH.

FIG. 2. Ultraviolet spectra of the bromo-complexes: as Fig. 1 but with Br in place of Cl.

The absorption curve of the green form of the diarsine dichloro-complex is shown in Fig. 1B together with the spectrum of the *trans*-dichloroethylenediamine complex (Fig. 1A). Fig. 1 also shows similar curves for the *cis*-complexes, and Fig. 2 for the bromo-complexes. The frequencies of the bands are listed in Tables 1 and 2. The assignment [12] of the intense charge-transfer bands in these spectra will be given in detail later, but it is clear that the absorption maximum at 16·4 × 10^3 cm.$^{-1}$ in Fig. 1B corresponds to a component of the

TABLE 1.

Ligand-field band Ia of *trans*-[CoB$_4$Cl$_2$]$^+$ complexes.

Base (B)	v (10^3 cm.$^{-1}$)	log ε	Ref.	Base (B)	v (10^3 cm.$^{-1}$)	log ε	Ref.
Pyridine	15·8	1·64	5	en	16·1	1·61	8, 9
NH$_3$	15·9	1·63	8, 9	Diarsine	16·4	1·85	This work

TABLE 2.

Absorption maxima of [CoB$_2$X$_2$]$^+$.

	Diarsine		en (ref. 9)			Diarsine		en (ref. 9)	
Isomer	v (10^3 cm.$^{-1}$)	log ε	v (10^3 cm.$^{-1}$)	log ε	Isomer	v (10^3 cm.$^{-1}$)	log ε	v (10^3 cm.$^{-1}$)	log ε
X = Cl					X = Br				
cis-	20·4	2·80	18·6	1·95	*cis*-	19·6	2·80	18·1	2·04
trans- ...	16·4	1·85	16·1	1·61	*trans*-	15·7	1·94	15·2	1·73

first spin-allowed ligand-field band. This frequency is close to that found for the *trans*-dichlorobis(ethylenediamine) complex in Fig. 1A, but is well removed from that found

[12] Dunn and Yamada, unpublished work.

for the *cis*-isomer (Fig. 1C). It is therefore concluded that the green isomer has a *trans*-configuration.

The purple dichloro-isomer has its first maximum at 20.3×10^3 cm.$^{-1}$ (Fig. 1D), and even a shoulder at 17.5×10^3 cm.$^{-1}$ which is similar to that of the *cis*-dichloroethylene-diamine analogue (Fig. 1C), so that it is shown conclusively to be the *cis*-isomer.

The isomeric bromides have also been prepared and analysed according to the above scheme, the same conclusions being reached, *viz.*, that the dark green isomer has the *trans*- and the purple isomer the *cis*-configuration.

EXPERIMENTAL

The green form of the salt [Co(diarsine)$_2$Cl$_2$]ClO$_4$ was prepared according to Nyholm's directions [13] from the green chloride [Co(diarsine)$_2$Cl$_2$]Cl and perchloric acid (Found: C, 30.0; H, 4.1. Calc. for C$_{20}$H$_{32}$As$_4$Cl$_3$CoO$_4$: C, 30.0; H, 4.0%).

The purple perchlorate [Co(diarsine)$_2$Cl$_2$]ClO$_4$ was prepared from the iodide [Co(diarsine)$_2$I$_2$]I. This iodide [13] (0.15 g.) was suspended in 80% ethanol (40 ml.), and an excess of silver acetate was added. The mixture was left overnight, filtered, and treated with 10N-hydrochloric acid (6 ml.) and concentrated perchloric acid (3 ml.). The purple crystals (0.085 g.) separated immediately and were filtered off after 15 min. and washed with water and ethanol. Purification was by recrystallisation from methanol containing a small amount of perchloric acid (Found: C, 30.1; H, 3.9%). The compound is slightly soluble in acetone, methanol, ethanol, and water but insoluble in benzene and chloroform.

The green complex [Co(diarsine)$_2$Br$_2$]ClO$_4$ was prepared from the bromide [13] as for the dichloro-complex and the purple *perchlorate* [Co(diarsine)$_2$Br$_2$]ClO$_4$ in the same way as the chloride but with hydrobromic instead of hydrochloric acid (Found: C, 27.1; H, 3.6. C$_{20}$H$_{32}$Br$_2$ClCoO$_4$ requires C, 27.0; H, 3.6%).

Spectrophotometric measurements were carried out with a Cary MS-11 spectrophotometer.

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[13] Nyholm, *J.*, 1950, 2071.