compared with trimethyl phosphite, even though it is a weaker base toward protons.[12]

We have attempted to use the catalytic effect of DMSO in preparative experiments to assist in the displacement of carbon monoxide from tungsten hexacarbonyl by arene, but without success. It is unlikely that other workers have overlooked effects as large as those shown here in kinetic studies on tungsten compounds, even though the phosphorus compounds may not always have been rigorously purified. The catalysis of arene displacements thus at present appears to be unique, although there may be some similarities to the catalysis observed for displacement of CO from $Fe(NO)_2(CO)_2$.[9]

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CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Proton Magnetic Resonance and Infrared Studies on Bis(o-phenylenebisdimethylarsine)cobalt(III) Complexes[1]

BY B. K. W. BAYLIS AND JOHN C. BAILAR, JR.

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The pmr and infrared spectra from 4000 to 80 K of several bis(diarsine)cobalt(III) complexes are reported. Deduction of structure (whether *cis* or *trans*) has been made on the basis of both types of spectra. Several new *cis* complexes are reported: $[Co(diars)_2(OAc)_2]BF_4$, $[Co(diars)_2CO_3]PF_6$, $[(Co(diars)_2HCO_3)_2HCO_3](BF_4)_3$, $[(Co(diars)_2HCO_3)_2HCO_3](ClO_4)_3$, $[Co(diars)_2(NO_3)_2]ClO_4$, and $[Co(diars)_2ox]PF_6$. Experimental frequency ranges from the literature for the bands in the infrared spectra of these acido groups, bound in various different ways, are tabulated. The nature of the bonding in the acetato, thiocyanato, carbonato, and oxalato groups has been determined by comparison of their infrared spectra with the ranges collected from the literature. The dimeric bicarbonato cation is quite unusual in that the bridging unit appears to be a bicarbonato group.

Introduction

Some years ago Jørgensen[2] proposed that complexes containing both hard and soft bases would be less stable than those containing only hard or only soft bases. Indeed, few complexes have been studied in which a hard acid such as Co(III) is bound to both hard and soft bases. We have prepared and characterized a series of cobalt(III) complexes containing two molecules of the soft base o-phenylenebisdimethylarsine (hereafter denoted diarsine (diars)) and various hard bases, either two monodentate anions or one bidentate anion. Nyholm and coworkers have prepared a number of complexes of the type $Co(diars)_2X_2^+$, where X = Cl, Br, I, and NCS[3] and acetate[4] ions, but the structures were determined only for the *cis*- and *trans*-dichloro and -dibromo isomers.[5,6] The series $Co(diars)_2NOX^+$, where X = Cl, Br, I, and NCS, has also been studied,[7] as have the visible and near-infrared spectra of the *trans*-dihalo complexes.[8]

The *cis* and *trans* isomers had been characterized using visible,[5] infrared,[7] and low-frequency infrared spectroscopy,[6] but the definitive assignment was the result of an X-ray study on the *trans*-dichloro complex.[6] We have found that the pmr spectra can clearly, quickly, and easily differentiate between isomers, even if the samples are somewhat impure. After ascertaining the structures of our complexes using pmr, we were able to assign a number of infrared bands and to show how the infrared spectra could be used in determining whether a pure sample of a given bis-diarsine complex was *cis* or *trans*. Further, we were able to determine the nature of the linkages between the diacido groups and the cobalt(III) ion from the infrared spectra.

Experimental Section

Reagents.—Most of the reagents used were reagent grade and were not further purified. The deuterated solvents used in recording the pmr spectra were obtained from the Merck Chemical Co. The o-arsanilic acid (one sample from Fluka A. G. Chemische Fabrik, "purum;" one from Schuchardt) was recrystallized. Deionized water and 99% undenatured ethanol were used. Almost all samples used for physical measurements had been washed with ethanol and then ether and dried under high vacuum (using a mercury diffusion pump) for 4 hr and gave good analyses. The complexes, particularly the *cis* isomers, are somewhat light sensitive, and most operations were carried out in blackened containers.

Diarsine.—The ligand o-phenylenebisdimethylarsine was prepared from o-arsanilic acid as described by Eberly and Smith[9] and Kalb.[10] From 81 g of starting material, 22.7 g of ligand, bp

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[1] Abstracted from a portion of a thesis submitted by B. K. W. Baylis to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the Ph.D. degree, 1968. The laboratory work was done at the Anorganisches-Chemisches Institut of the Technische Hochschule, Munich, West Germany.

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142–144° (12 mm), was prepared. *Anal.* Calcd for $C_{10}H_{16}As_2$: C, 41.98; H, 5.64. Found: C, 42.08; H, 5.67.

trans-**[Co(diars)$_2$Cl$_2$]Cl.**—This complex was prepared from $CoCl_2 \cdot 6H_2O$ and diarsine following the procedure of Nyholm.[3] *Anal.* Calcd for $C_{20}H_{32}As_4Cl_3Co$: C, 32.57; H, 4.37. Found: C, 32.74; H, 4.43. The green crystals melted at 308.5° after some decomposition.

trans-**[Co(diars)$_2$Cl$_2$]ClO$_4$.**—The perchlorate salt was prepared by dissolving 0.58 g of the chloride salt in about 100 ml of hot ethanol, cooling, adding 5 ml of concentrated $HClO_4$, and allowing the mixture to stand for 36 hr. The green crystals were collected and washed and dried as above. *Anal.* Calcd for $C_{20}H_{32}As_4Cl_3CoO_4$: C, 29.98; H, 4.02. Found: C, 30.34; H, 4.08. No melting point was taken of this or of any other of the perchlorate salts.

trans-**[Co(diars)$_2$I$_2$]I.**—This complex was prepared from *trans*-[Co(diars)$_2$Cl$_2$]Cl following the procedure of Nyholm.[3] *Anal.* Calcd for $C_{20}H_{32}As_4CoI_3$: C, 23.74; H, 3.18. Found: C, 24.50; H, 3.17. No melting point below 315° was observed for the almost black crystals.

cis-**[Co(diars)$_2$Cl$_2$]ClO$_4$.**—This purple complex was prepared from *trans*-[Co(diars)$_2$I$_2$]I, AgOAc, and HCl following the procedure of Peloso and Tobe.[11] *Anal.* Calcd for $C_{20}H_{32}As_4Cl_3CoO_4$: C, 29.98; H, 4.02. Found: C, 30.30; H, 4.31.

trans-**[Co(diars)$_2$Br$_2$]Br.**—Into a hot, filtered solution of 0.36 g of *trans*-[Co(diars)$_2$Cl$_2$]Cl in 100 ml of ethanol was filtered a hot solution of 1.6 g of LiBr in 10 ml of ethanol. The reaction solution was concentrated somewhat and then refluxed for 4 hr. After the solution was allowed to cool and stand, green crystals formed which were collected, recrystallized from hot methanol, and treated as above. *Anal.* Calcd for $C_{20}H_{32}As_4Br_3Co$: C, 27.59; H, 3.70. Found: C, 27.61; H, 3.81. No definite melting point was observed up to 319°.

trans-**[Co(diars)$_2$(OAc)$_2$]ClO$_4$.**—This red complex was prepared from $Co(OAc)_2 \cdot 4H_2O$ and diarsine following the procedure of Burstall and Nyholm.[4] *Anal.* Calcd for $C_{24}H_{38}As_4ClCoO_8$: C, 33.97; H, 4.51. Found: C, 33.30; H, 4.51.

cis-**[Co(diars)$_2$(OAc)$_2$]BF$_4$.**—A suspension of 0.5 g of [Co(diars)$_2$I$_2$]I in 25 ml of 80% ethanol was stirred overnight with 1.2 g of AgOAc. To the filtered solution was added 1 ml of HOAc. After evaporation to dryness at room temperature with a water aspirator, enough methanol was added to dissolve the red residue. A filtered solution of 0.11 g of $NaBF_4$ in 40 ml of methanol was added. The first crystals which formed at room temperature were *trans* and were removed. The red *cis* complex was precipitated with ether, collected, and treated as above. *Anal.* Calcd for $C_{24}H_{38}As_4BCoF_4O_4$ (*cis* isomer): C, 34.48; H, 4.58. Found: C, 34.21; H, 4.63.

cis-**[Co(diars)$_2$CO$_3$]PF$_6$.**—One gram of *trans*-[Co(diars)$_2$I$_2$]I was triturated with Ag_2CO_3 (prepared from 2.4 g of $AgNO_3$) in 10 ml of ethanol for 20 min. The silver salts were filtered and washed with more ethanol. The combined filtrate and washings were evaporated at room temperature to about 8 ml using a water aspirator vacuum. A filtered solution of 0.1 g of NH_4PF_6 in 3 ml of methanol was added, and only after the walls of the container were scratched did any precipitate form. After 3 hr this was collected, recrystallized from warm methanol, and treated as above. The yield was 0.64 g. *Anal.* Calcd for $C_{21}H_{32}As_4CoF_6O_3P$: C, 30.17; H, 3.86; Co, 7.05; As, 35.84; O, 5.74; P, 3.70; F, 13.64. Found: C, 30.27; H, 4.04; Co, 7.10; As, 31.9; O, 5.6; P, 3.69; F, 12.8. The orange crystals began to melt at 142°.

cis-**[(Co(diars)$_2$HCO$_3$)$_2$HCO$_3$](ClO$_4$)$_3$.**—One gram of *trans*-[Co(diars)$_2$I$_2$]I in 36 ml of 80% ethanol was stirred with Ag_2CO_3 for 24 hr. The red-orange solution was filtered and a saturated solution of $NaClO_4$ was added. The resulting precipitate was redissolved in hot ethanol and the solution was filtered and allowed to stand from 4 hr to 4 days. The orange crystals were collected and treated as above. *Anal.* Calcd for $C_{43}H_{67}As_8Cl_3Co_2O_{21}$: C, 29.62; H, 3.87; Co, 6.61. Found (the ranges for C and H are for five different samples): C, 29.44–29.99; H, 3.62–4.20; Co, 6.86.

cis-**[(Co(diars)$_2$HCO$_3$)$_2$HCO$_3$](BF$_4$)$_3$.**—One gram of *trans*-[Co(diars)$_2$I$_2$]I was triturated with Ag_2CO_3 in 10 ml of ethanol for 20 min in an ice-cold mortar. The silver salts were filtered and washed with ethanol, and the combined filtrate and washings were evaporated to dryness at room temperature with a water aspirator vacuum. The residue was dissolved in 5 ml of ethanol, and the solution was filtered and added to a saturated solution of 0.11 g of $NaBF_4$ in 40 ml of ethanol. After 1 day, the precipitate was collected and recrystallized one or more times from methanol using a small amount of ether. After precipitating overnight in the cold, the orange crystals were collected and treated as above. Yields were around 0.65 g. *Anal.* Calcd for $C_{43}H_{67}As_8B_3Co_2F_{12}O_9$: C, 30.28; H, 3.96; Co, 6.75; As, 35.14; F, 13.36; O + B, 10.34. Found (the ranges for C and H are for six different samples): C, 30.03–30.70; H, 3.87–4.39; Co, 6.70; As, 34.3; F, 13.5. The remaining 10.5% was assumed to be oxygen and boron. The crystals began to melt at 216°.

trans-**[Co(diars)$_2$(NCS)$_2$]NCS.**—A concentrated solution of *cis*-[(Co(diars)$_2$HCO$_3$)$_2$HCO$_3$](ClO$_4$)$_3$ was treated with NH_4SCN for 2 hr on a steam bath. The red crystals which formed upon standing at room temperature were collected and treated as above. *Anal.* Calcd for $C_{23}H_{32}As_4CoN_3S_3$: C, 34.30; H, 4.06. Found: C, 34.28; H, 4.07. The crystals began to lose form at 203°, and by 228° only a black tar remained.

cis-**[Co(diars)$_2$(NO$_3$)$_2$]ClO$_4$.**—Solid [(Co(diars)$_2$HCO$_3$)$_2$HCO$_3$](ClO$_4$)$_3$ was added to 2 *N* HNO_3, and the precipitate which formed immediately was ground against the walls of the container. After 3 hr the crystals were collected and dissolved in nitromethane. Ether was added and the clear solution was placed in a refrigerator overnight. The red prisms were collected and treated as above. *Anal.* Calcd for $C_{20}H_{32}As_4ClCoN_2O_{10}$: C, 28.11; H, 3.78; N, 3.28. Found: C, 28.43; H, 3.97; N, 3.37.

cis-**[Co(diars)$_2$ox]PF$_6$.**—One gram of [Co(diars)$_2$I$_2$]I was triturated with Ag_2ox (made from 2.4 g of $AgNO_3$) in 10 ml of ethanol for 45 min. The silver salts were filtered and washed with more ethanol. The combined filtrate and washings were concentrated under a water aspirator vacuum to about 10 ml. This solution was filtered, using much filter aid, into a filtered solution of 0.24 g of NH_4PF_6 in methanol. After the addition of ether, the solution was allowed to stand in a freezer. The precipitate was collected and recrystallized from methanol. After standing 4 hr in a freezer, the precipitate was collected and treated as before. *Anal.* Calcd for $C_{22}H_{32}As_4CoF_6O_4P$: C, 30.58; H, 3.73. Found: C, 30.68; H, 3.98. The orange crystals began to melt at 208°.

Spectra.—The pmr spectra were obtained by I. Reithebuch and K. E. Schwarzhans on a Varian A-60 analytical spectrometer. Tetramethylsilane was used as an internal standard whenever possible; otherwise it was the external standard.

Infrared spectra in the 4000–650-K region were recorded by R. Koneberg on a Perkin-Elmer Model 21 spectrometer with NaCl optics. Both KBr pellets and Nujol and Hostaflon (a low molecular weight polymeric perfluoroethylene made by Hoechster Farben, AG, Frankfurt am Main) mulls were used. In the region 700–33 K, a Beckman IR-11 grating spectrometer, operated by E. Hotop, was used. The samples were in Nujol mulls suspended between polyethylene plates. Some spectra were recorded for the region 4000–200 K with a Beckman IR-12 grating spectrometer.

The visible and ultraviolet spectra were obtained with a Beckman DK-2 ratio recording spectrometer and with a Perkin-Elmer Spectracord 4000 A. The solvents used were refluxed over a drying agent under nitrogen and were distilled and stored under nitrogen.

Conductivity.—These measurements were made on a Siemens conductivity meter, Type LBR; the cell used had a cell constant of 0.6. The acetone used was fractionally distilled.

Microanalyses.—Analyses for C, H, N, and Co were performed by C. Hillmer and M. Barth of the Institut für Anorganische Chemie of the Technische Hochschule in Munich. Analyses

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[11] A. Peloso and M. L. Tobe, *J. Chem. Soc.*, 5063 (1964).

TABLE I

METHYL RESONANCES OF BIS(DIARSINE)COBALT(III) COMPLEXES

Compound	Solvent	Methyl resonances, ppm				
Diarsine						0.92
trans-$[Co(diars)_2(OAc)_2]ClO_4$	$(CD_3)_2SO$		1.81			1.36[a]
trans-$[Co(diars)_2Cl_2]Cl$	D_2O		2.47			
trans-$[Co(diars)_2(NCS)_2]NCS$	$(CD_3)_2SO$		2.16			
trans-$[Co(diars)_2I_2]I$	$(CD_3)_2SO$		2.39			
trans-$[Co(diars)_2I_2]I$	CD_3OD		2.48			
cis-$[Co(diars)_2(OAc)_2]BF_4$	D_2O	2.75	2.57	2.43	1.38	1.81[a]
cis-$[Co(diars)_2Cl_2]ClO_4$	CH_3OH	2.06	1.92	1.56	1.16	
cis-$[Co(diars)_2Cl_2]ClO_4$	CD_3NO_2	2.30	2.21	1.76	1.34	
cis-$[Co(diars)_2CO_3]PF_6$	$(CD_3)_2SO$	2.32	1.77	1.73	1.29	
cis-$[(Co(diars)_2HCO_3)_2HCO_3](BF_4)_3$	$(CD_3)_2SO$	2.34	1.79	1.75	1.30	
cis-$[(Co(diars)_2HCO_3)_2HCO_3](BF_4)_3$	D_2O	2.81	2.31	2.18	1.97	
cis-$[Co(diars)_2ox]PF_6$	$(CD_3)_2SO$	2.32	1.77	1.68	1.27	
cis-$[Co(diars)_2(NO_3)_2]ClO_4$	CD_3NO_2	2.39	2.22	1.60	1.03	

[a] Acetato methyl resonance.

for P, F, As, and O were performed in the laboratory of W. Pfad at the Badische Anilin- und Soda-Fabrik AG.

Results and Discussion

Proton Magnetic Resonance Spectra.—The methods, visible and infrared spectroscopy,[5-7] which had been used previously to determine the stereochemistry of these complexes require that the samples be very pure and that both *cis* and *trans* isomers be available for comparison. Proton magnetic resonance is more sensitive to the differences in environments of the methyl groups in *trans* and *cis* isomers, making the spectra of the isomers (see Table I) more easily distinguished.

It is obvious from a model of *trans*-$Co(diars)_2I_2^+$ that all methyl groups in the *trans* isomers are in equivalent environments. Hence only one methyl resonance is expected. Only one is found for the samples of the diiodo, diisothiocyanato, and *trans*-dichloro complexes made following the directions given by Nyholm.[3] Our sample of the diacetato complex prepared by Nyholm's method[4] gives two methyl resonances, one with intensity four times that of the other. The weaker resonance is caused by the methyl groups on the two acetato ligands; the stronger, by the eight methyl groups in the two diarsine ligands.

The pmr spectrum of the *cis*-dichloro complex contains four methyl resonances. The four methyl groups on each diarsine molecule in the *cis* isomer are in four different environments, and thus four methyl resonances are to be expected for this complex. The pmr spectra of the carbonato and oxalato complexes contain four methyl resonances, as do the dichloro and dinitrato complexes prepared by acidification of the carbonato complex. The diacetato complex prepared by rapid precipitation from the reaction mixture shows five methyl resonances, four caused by the two diarsine ligands and one caused by the two acetato groups. Thus all of these complexes have been shown to be of the *cis* configuration.

Course of Reactions.—It is evident from the above that *cis* isomers are actually quite common among the bis-diarsine complexes. The difficulty in collecting them has come from the fact that if the compounds are allowed to precipitate slowly, only the *trans* isomers are recovered because of lower solubility or greater thermodynamic stability. In the dichloro case, at least, the latter is more likely as indicated by the fact that Peloso and Tobe[11] were able to follow the *cis* to *trans* conversion spectrophotometrically.

To obtain *cis* complexes from *trans* starting material, it is necessary to use a reagent which completely removes the leaving group from the starting complex. The reaction of silver salts with *trans* starting materials has always resulted in *cis* products.

$$trans\text{-}Co(diars)_2X_2^+ + 2AgY \longrightarrow cis\text{-}Co(diars)_2Y_2^+ + 2AgX$$

$$trans\text{-}Co(diars)_2X_2^+ + Ag_2Z \longrightarrow cis\text{-}Co(diars)_2Z^+ + 2AgX$$

For example, the *cis*-dinitrato, -carbonato, -oxalato, and -diacetato derivatives were prepared from *trans*-diiodo and -dichloro complexes in this way. In general, if the leaving group is not removed from the vicinity of the *trans* starting material, the product is also *trans*

$$trans\text{-}Co(diars)_2X_2^+ + 2Y^- \longrightarrow trans\text{-}Co(diars)_2Y_2^+ + 2X^-$$

The kinetics of this reaction in methanol where X = Cl and Y = Cl or NCS have been studied by Dolcetti and Peloso.[12] They proposed an intermediate of the type $Co(diars)_2Cl_2(CH_3O)$ to explain their results for the chloride exchange. If the leaving group should, indeed, remain in close proximity to its former bonding position, it seems reasonable that it would thus keep this position available for the entering group. If, however, the leaving group is removed from the vicinity by a silver ion, a slight shift in position of the diarsine ligands to form a trigonal-bipyramidal intermediate could well allow the methyl groups to shield the former *trans* position from attack. The entering group would then meet less resistance upon attacking near the remaining acido group (hence forming a *cis* product) than in the old *trans* position. Attachment of the silver ion to one of the halo groups, blocking attack from this direction by the entering group, could also cause the formation of a *cis* product.[13,14]

(12) G. Dolcetti and A. Peloso, *Gazz. Chim. Ital.*, **97**, 230 (1967).

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TABLE II
INFRARED SPECTRA OF BIS(DIARSINE)COBALT(III) COMPLEXES IN THE REGION 700–3100 K

Assignment[a]	$C_6H_4[As(CH_3)_2]_2$[a]	*trans* complexes	*cis* complexes
b_2 fundamental	692 w[b]	700–702 w	701–707 w
a_2 fundamental	719 w	715–717 vw	712–714 vw
b_1 fundamental	744 s	752–784 ms	753–766 ms
b_1 combination band	785 w	813 vw	
b_1 combination band	826 vw	833 w	824–833 w
$\rho(CH_3)$	846 s	846–860 sh 864–873 s	846–864 w 864–873 s 874–889 ms
a_2 fundamental	865 sh	898–902 m	900–901 m
$\rho(CH_3)$	885 s	910–919 ms	909–921 ms
b_1 fundamental	941 w	953–958 w	968 w
a_2 fundamental	980 vw	971 w	
b_2 fundamental	1024 w	1018 w	
a_1 fundamental	1034 m	1030–1033 w	1027–1032 w
a_1 fundamental	1090 m	1107–1110 m	1105–1108 m
b_1 combination band	1119 w	1128–1129 vw	1128–1130 vw
a_1 fundamental	1160 w	1158–1172 w	1158–1169 w
b_2 fundamental			1218 vw
b_2 fundamental	1235 sh	1248 w	1248 sh
$\delta_a(CH_3)$	1250 ms	1250–1262 mw	1257–1265 w
$\delta_s(CH_3)$	1261 m	1274–1280 mw	1273–1287 mw
$\delta_a(CH_3)$	1421 s	1409–1418 ms	1400–1418 m
a_1 and b_2 fundamental	1441 m	1428–1436 m 1448–1458 m	1439–1451 mw
b_2 combination band	1560 w		1543 vw
b_2 fundamental	1563 w	1550–1563 w	1561–1563 w
$\nu_s(CH_3)$	2900 s	2870–2890 w	2880–2960 w
$\nu_a(CH_3)$	2980 s		
	3040 m	2914–2960 w	2980–3098 w
a_1 and b_2 fundamental	3058 sh		

[a] The assignments and frequencies for the free ligand are from ref 16 and 17. The symbol ρ indicates a rocking mode, δ_a an antisymmetric deformation, δ_s a symmetric deformation, ν_a an antisymmetric stretch, and ν_s a symmetric stretch. [b] Intensities are denoted throughout this paper as: w, weak; m, medium; s, strong; v, very; sh, shoulder.

TABLE III
INFRARED SPECTRA OF BIS(DIARSINE)COBALT(III) COMPLEXES IN THE REGION 80–700 K

Assignment[a]	$C_6H_4[As(CH_3)_2]_2$[a]	*trans* complexes	*cis* complexes[b]
a_2 fundamental	94 s	89–101 m–s	105 m
a_1 fundamental	125 s	118–122 w–m	119 m
b_1 fundamental	188 m	177–180 w–m	177 mw
$\delta(CH_3\text{–}As\text{–}CH_3)$	231 m	242–264 w–m	257 mw
b_2 fundamental	278 s	275–295 s	280 s
$\nu[As\text{–}C(C_6H_5)]$	344 s	362–376 s	366–369 s
		375–381 s	379–385 s
		391–407 w	
b_1 fundamental	433 s	437–443 s	433–435 s
		500–523 w	470–471 m–w
		541–559 w–m	533 w
$\nu_s[As\text{–}C(CH_3)]$	568 s	591–604 s	599–600 s
$\nu_a[As\text{–}C(CH_3)]$	576 s	607–620 m–s	620 m
a_1 fundamental	645 w	665–669 w	669 w

[a] The assignments and frequencies for the free ligand are from ref 16 and 17. The symbol δ indicates a deformation, ν_a an antisymmetric stretch, and ν_s a symmetric stretch. [b] Only one *cis* complex was studied in the region 80–300 K and only two were studied in the region 300–700 K.

It has been noted that the *trans* isomers seem to be generally more stable than the *cis* isomers, in that, in time, most *cis*-diarsine complexes convert to the *trans* isomers. Presumably, although the entering group encounters less steric resistance upon entering a trigonal-bipyramidal intermediate *cis* to an acido group, the crowding of the *cis* complex is sufficient to make it relatively labile. Once the group succeeds in entering the *trans* position which would statistically happen one time in three, if the steric effects were neglected, the resulting complex is more stable than the *cis* complex. Peloso[15] has suggested an intramolecular mechanism involving no release of acido groups for this isomerization.

The products of reactions with *cis* starting materials in acidic solution were found to be *cis*

$$cis\text{-}Co(diars)_2X_2^+ + 2Y^- \longrightarrow cis\text{-}Co(diars)_2Y_2^+ + 2X^-$$

where $X = OAc$, $Y = Cl$; and $X_2 = CO_3$, $Y = Cl$, NO_3, and NCS. If the product is not precipitated very rapidly from the solution, the *cis* isomer is converted to the *trans* form. Hence, in the case of the isothiocyanato complex, the only pure samples ever collected were allowed to precipitate slowly and were *trans*. The samples which were precipitated rapidly were always mixtures, as indicated by the infrared spectra.

Infrared Spectra.—The infrared spectra of these complexes are very complicated owing to the complexity of the diarsine ligand. Fortunately, the diarsine bands are sharp and bonding does not greatly change their positions. The positions of the bands for the free ligand (data and assignments are taken from Rodley[16,17]) and for the bound ligand in *cis* and *trans* complexes are given in Table II for the region 3100–700 K and in Table III for the region 700–80 K.

It can be seen from Table II that there is a consistent difference between the spectra of *cis* and *trans* complexes in the region 920–840 K, where the methyl rocking vibrations occur. The *cis* isomers usually have more bands than the *trans* in this region, and, in particular, they have a band between 874 and 889 K where the *trans* isomers do not. However, the *cis* isomers have so many bands in this region that, unless the sample is free of *trans* impurity and the resolution of the instrument is quite good, only one broad band may be seen in the region 890–840 K. In fact, Feltham and Nyholm[7] diagnosed their spectra on the basis that *cis* isomers give single bands at 860 and 920 K, whereas in *trans* isomers these bands are each split into two bands. This latter generalization is true only of chloride and bromide salts. The perchlorate and iodide salts of the *trans* isomers show a total of only two bands in this region, and the thiocyanate salt shows only three.

The behavior of the As–C stretching vibrations for both the methyl and phenyl groups is especially noteworthy. In both cases, the energies of the As–C stretches are lowered by increasing the weight of the complex. That is, these bands occur at decreasing energies for the series of complexes dichloro, dibromo, and diiodo. This trend is as would be predicted from considerations of the effect of changes in mass on the energies of vibrational transitions.

Diacetato Complexes.—The pmr spectrum of a

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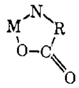
(15) A. Peloso and G. Dolcetti, *J. Chem. Soc., A*, 1506 (1969).

(16) G. A. Rodley, Ph.D. Thesis, University College, London, 1963.

(17) J. H. S. Green, W. Kynaston, and G. A. Rodley, *Spectrochim. Acta*, **24A**, 853 (1968).

TABLE IV
INFRARED SPECTRA OF THE $RCOO^-$ GROUP

Compounds[a]	Band freq, K				Δν, K	Ref
RCO_2^-	1637–1530 s	1420–1300 m–s	777–607 s	694–608 s	235–119	*c–h*
$CH_3CO_2^-$	1578–1530 s	1414–1395 s	671–646	660–611	164–119	*c, f, h, i*
$MRCO_2$	1630–1575 s	1385 s	705 m	617 m	225	*e, j*
MOC(O)R	1684–1520 s	1460–1297 s[b]	762–640	616–610	306–86	*f, h, k–m*
$MOC(O)CH_3$	1655–1520 s	1460–1297 s	762–640	616–610	281–86	*f, h, k, l*
MO_2CR	1577–1505	1470–1425	686–670		152–60	*f, k, n*
MOC(R)OM	1639–1567 s	1489–1408 m–s			180–75	*f, k, o, p*
$MOC(CH_3)OM'$	1631–1590	1449–1395	674		231–159	*f, q*
	1659–1560 s[b]	1435–1347 s[b]	790–708 w–m	643–490 m–s	292–155	*d, e, r–y*
RCO_2H	1740–1668 s	1320–1211 s			~500–327	*c, e, j, s, z*
$MRCO_2H$	1750–1690 m–s[b]	1262–1238 s	704–695 m	594–585 s	475–446	*e, j, s–u, y*
trans-$CoD_2(OAc)_2^+$	1616 s, 1602 s	1368 s, 1314 s	780 ms, 688 m		278	*aa*
cis-$CoD_2(OAc)_2^+$	1622 s, 1607 s	1376 s, 1330 s, 1321 s	672 m		246	*aa*

[a] D = diarsine. [b] Sometimes two bands are reported in this region. [c] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958. [d] I. Nakagawa, R. J. Hooper, J. L. Walter, and T. J. Lane, *Spectrochim. Acta*, **21,** 1 (1965). [e] J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **29,** 2561 (1967). [f] N. F. Curtis, *J. Chem. Soc.*, *A*, 1579 (1968). [g] Reference 19, pp 199, 202, 204. [h] Reference 18. [i] Reference 19, p 199. [j] Reference 19, p 206. [k] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965). [l] S. Onaka, T. Iwamoto, Y. Sasaki, and S. Fujiwara, *Bull. Chem. Soc. Japan*, **40,** 1398 (1967). [m] R. Pastorek and F. Brezina, *Monatsh. Chem.*, **98,** 156 (1967). [n] R. S. P. Coutts and P. C. Wailes, *Australian J. Chem.*, **20,** 1579 (1967). [o] G. Rouschias and G. Wilkinson, *J. Chem. Soc.*, *A*, 465 (1966). [p] Reference 19, p 200. [q] R. W. Brandon and D. V. Claridge, *Chem. Commun.*, 677 (1968). [r] Reference 19, p 204. [s] D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75,** 4574 (1953). [t] D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78,** 716 (1956). [u] R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1,** 174 (1962). [v] R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42,** 2590 (1965). [w] G. W. Watt and D. S. Klett, *Inorg. Chem.*, **3,** 782 (1964). [x] G. W. Watt and J. F. Knifton, *ibid.*, **7,** 1159 (1968). [y] M. Mori, M. Shibata, E. Kyuno, and H. Nakajima, *Bull. Chem. Soc. Japan*, **29,** 887 (1956). [z] D. Mücke, G. Geppert, and L. Kipke, *J. Prakt. Chem.*, **9,** 16 (1959). [aa] This work.

sample prepared by the method of Burstall and Nyholm[4] showed only two methyl resonances, one of which was due to the acetato methyl group. Hence it appears that theirs was a *trans* complex. Dunn, Nyholm, and Yamada[5] prepared the *cis*-dichloro complex by stirring the diiodo complex with AgOAc and then adding HCl. Instead of carrying through the conversion to the *cis*-dichloro complex, we precipitated the acetato complex and determined from the pmr spectrum that it is a *cis*-diacetato complex.

Table IV lists ranges that have been reported for the vibrations of carboxylic acids in different bonding situations. This general list includes amino acids which can be bound to a metal ion other than through the carboxylate group. The range given for the highest energy for MOC(O)R describes complexes with quite weak bonding. For a more strongly bound metal ion such as Co(III) or Cr(III), the range is probably about 1680–1600 K.

The bands in the infrared spectrum of *trans*-[Co(diars)$_2$(OAc)$_2$]ClO$_4$, after deletion of the diarsine and anion vibrations, are reported in Table IV. The doublet near 1600 K is the asymmetric carboxylate stretch ν_a(COO) and that at 1368 K is the symmetric ν_s(COO). The band at 688 K and probably also that at 780 K are caused by bending modes of the carboxylate group. The band at 1314 K is quite possibly a bending mode of the acetato methyl group, for which a range of 1333–1316 K has been reported for monodentate acetato groups.[18] Methyl and methylene twisting or wagging modes appearing in this region are often of high intensity, possibly due to Fermi resonance. The difference ν_a(COO) − ν_s(COO) (in the column in Table IV labeled Δν) has been widely proposed for use as an indication of bonding type for carboxylato complexes, as well as for carbonato, nitrato, and sulfato complexes (for example, see Nakamoto[19]). The difference between the carboxylate stretches for *trans*-[Co(diars)$_2$(OAc)$_2$]ClO$_4$ is 278 K. This difference is quite reasonable for a strongly bound monodentate acetato group, as are all of the bands assigned to the acetato group for this complex (compare with Table IV). The bands in the *cis* complex are similar, but the presence of some *trans* isomer has broadened many of the diarsine bands, especially those in the 900–750-K region, and no band near 780 K can be distinguished.

Carbonato Complexes.—Four anions, two solvents, and two slightly different methods of preparation were used in the attempt to prepare a carbonato complex. The analysis of the hexafluorophosphate salt indicates the complex to be [Co(diars)$_2$CO$_3$]PF$_6$. Its pmr spectrum is that of a *cis* complex, and the infrared spectrum, after deletion of diarsine and anion bands, is very similar to that due to the carbonato group in $((C_6H_5)_3P)_2PtCO_3$ (see Table V). An X-ray crystal structure of the latter[20] has confirmed the presence of a bidentate carbonato group. These two spectra differ from those of other bidentate carbonato complexes in which there

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[18] J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, **21,** 1043 (1965).

[19] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 161, 198, 204.

[20] F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *Chem. Commun.*, 408 (1967).

Table V
Infrared Spectra of the Carbonate Group

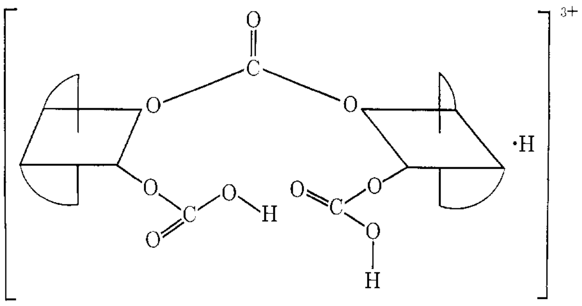
Compound	Band freq, K							Ref
CO_3^{2-}	1460–1390 s		1080–1060 w	885–850 m–s	745–680 m–s			*a–e*
$MOCO_2$	1495–1445 s	1373–1351 s	1072–1047 w	880–848 m–s	778–727 w	699–673 w	362–338 m–s	*a–d, f–h*
MO_2CO	1643–1615 1615–1575 s	1288–1255 s	1044–1015 w–m	885–821 w–s	770–742 m	683–667 m	488–382 m–s 395–318 s	*c–i*
$Pt(P(C_6H_5)_3)_2CO_3$	1680	1180	980	875	760			*j*
MO(O)COM	1480 s	1340 s	1030 m	830 m	760 w	675 w		*d*
HCO_3^-	1660–1655 s 1630–1620 s	1410–1400 s 1370–1295 s	1050–1010 w–s 1000–990 s	840–830 s		705–698 s		*k, l*
Dimeric HCO_3^-	1682 m 1618 s	1405, 1367 s 1283 s	1029 s 1001 m	832 w 830 m		698 m, 676 w 655 m, 635 s		*l, m*
Salts								
PF_6^-	1675 s 1627 ms	1190 m	982 mw	890 sh	732 m	665 m	449 m 332 m	*n*
BF_4^-	1669 s 1633 ms	1220 mw	Anion	821 m	767 m 744 m	670 w	Not investigated	*n*
ClO_4^-	1665 s 1630 ms	1215 mw	1000 w	820 m	764 m 742 m	Not investigated		*n*

[a] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36,** 339 (1962). [b] H. Elliott and B. J. Hathaway, *Spectrochim. Acta*, **21,** 1047 (1965). [c] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79,** 4904 (1957). [d] V. E. Sahini and M. Damaschin, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **8,** 193 (1963). [e] H. Siebert, *Z. Anorg. Allgem. Chem.*, **298,** 51 (1958). [f] J. A. Goldsmith and S. D. Ross, *Spectrochim. Acta*, **24A,** 993 (1968). [g] J. A. Goldsmith, A. Hezel, and S. D. Ross, *ibid.*, **24A,** 1139 (1968). [h] Reference 19, p 160. [i] M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **28,** 1659 (1966). [j] C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Commun.*, 407 (1967). [k] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24,** 1253 (1952). [l] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 3137 (1958). [m] K. Nakamoto, Y. A. Sarma, and H. Ogoshi, *J. Chem. Phys.*, **43,** 1177 (1965). [n] This work.

is an opportunity for hydrogen bonding to the carbonato group. In fact, the X-ray crystal structure study of $[Co(NH_3)_4CO_3]Br$ indicates considerable hydrogen bonding between the nonbound oxygen and ammines on adjacent complexes.[21] It has often been noted that hydrogen bonding changes the frequencies of the carbonyl vibrations.

The cation precipitated by the perchlorate and tetrafluoroborate anions is not a simple bidentate carbonato complex. The analyses correspond to the formula $Co_2As_8C_{43}H_{67}O_9(anion)_3$. Conductivity measurements in acetone indicate a molecular weight of about 1800 if a 3:1 salt is assumed, and the molecular weight calculated on the basis of the total analysis of the tetrafluoroborate salt (assuming two Co per molecule, eight As per molecule, etc.) is around 1750. The pmr spectra of both salts are very similar to that of the PF_6^- salt and indicate that both pairs of diarsine molecules are in *cis* positions. No protons other than the phenyl and methyl protons are observed in the room-temperature pmr spectra.

Carbon dioxide is evolved upon acidification, indicating the presence of a carbonato or bicarbonato group. The infrared spectra of the perchlorate and tetrafluoroboronate salts are identical, except for the anion bands, and similar to that of the hexafluorophosphate salt (see Table V). The visible spectra of the three salts are also almost identical. The structure which is proposed to fit these data contains two monodentate bicarbonato groups and a bridging carbonato group. The position of the third proton is not known at present, but it may be on the bridging carbonato group. If it were hydrogen bound between the bicarbonato groups, between one and an anion, or between two anions (see Faithful, *et al.*,[22] for precedents), this proton should be fairly acidic. However, attempts to titrate the protons indicated a low acidity with a pK_a of around 10.8. Hence the structure of the dimer cannot as yet be considered clarified.



Diisothiocyanato Complex.—It was of interest to determine whether the complex Nyholm[3] had prepared and Peloso[11,12,15] had studied was *cis* or *trans*, especially since Peloso was studying its formation from the *cis*-dichloro complex. We prepared samples by Peloso's method and by heating the *cis*-bicarbonato complex with NH_4SCN. The only pure samples obtained were those which precipitated slowly, and these showed only one methyl resonance in the pmr spectrum. The visible spectrum of this sample was identical with the spectrum reported by Peloso, and hence it is assumed that his product was also the *trans* isomer.

The other question to be resolved was that of the type of bonding of the NCS group. Table VI gives the ranges of frequencies shown by the thiocyanate group in various different bonding situations. It can be seen that the C–S stretching frequency [denoted ν(CS)] is the best for determining bond type. How-

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[21] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 586 (1962).

[22] B. D. Faithful, R. D. Gillard, D. G. Tuck, and R. Ugo, *ibid.*, *A*, 1185 (1966).

TABLE VI
INFRARED SPECTRA OF THE NCS GROUP

Compounds	ν(CN), K	2δ(NCS), K	ν(CS), K	δ(NCS), K	ν(MN), K	M	Ref
NCS^-	2070–2041 s	970–926 w–s	764–735 w	484–480			*a*, *b*, 7
MNCS	2167–2042 s		880–758 w–m	497–450 w–s			*a*, *b*, *c–g*
	2110–2045 s		847–758 w–m	497–467 m–s	382–313 m–s	Cr(III)	*f*, *g*
	2167–2065 s		840–787 w			Co(III)	*a*, *b*, *j*
	2083 s, 2051 s		833–820 m			Co(III)	24
MSCN	2132–2046 s	923–920 s 900–847 w	760–690 w	479–400 w			*a*, *c*, *d*, *h*, *i*
MNCSM′	2182–2129 s	942–922 s 897–863 w	799–737 w				*a*, *k*
trans-$CoD_2(NCS)_2$	2086 s		827 mw	467 m	338 m		*l*
·NCS	2042 ms		744 w	480 mw			

[a] M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81,** 6412 (1959). [b] M. E. Baldwin, *J. Chem. Soc.*, 471 (1961). [c] J. Lewis, R. S. Nyholm, and P. W. Smith, *ibid.*, 4590 (1961). [d] I. Bertini and A. Sabatini, *Inorg. Chem.*, **5,** 1025 (1966). [e] C. Pecile, *ibid.*, **5,** 210 (1966). [f] M. A. Bennett, R. J. H. Clark, and A. D. J. Goodwin, *ibid.*, **6,** 1625 (1967). [g] M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc.*, *A*, 592 (1967). [h] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83,** 4157 (1961). [i] M. J. Hudson, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, *A*, 40 (1968). [j] I. Stotz, W. K. Wilmarth, and A. Haim, *Inorg. Chem.*, **7,** 1250 (1968). [k] Reference 19, p 175. [l] This work.

TABLE VII
INFRARED SPECTRA OF THE NITRATE GROUP

Compounds	Band freq, K					Ref
NO_3^-	1400–1280 s		1068–1018 w	840–817 m	736–700	*a–d*
$MONO_2$	1600–1450 m–s[t]	1290–1220 s[t]	1034–970 m–s	806–780 w–s[t]	751–727 m	*a–c*, *e–j*
MO_2NO	1663–1462 s[t]	1346–1158 m–s[t]	1042–965 w–s[t]	835–804 w–s	785–738 m–s	*f*, *j–r*
MON(O)OM	1630 s, 1550 sh	1280, 1226 s 1147 w	1065 s	863, 805 s	767, 715 s	*c*
cis-$CoD_2(NO_3)_2^+$	1563 w, 1483 s	1387 w, 1340 m 1269 s	1008 s, 995 s	793 w	763 m, 714 w	*s*

[a] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Inorg. Nucl. Chem.*, **8,** 75 (1958). [b] A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, **93,** 687 (1963). [c] C. C. Addison and N. Logan, *Advan. Inorg. Chem. Radiochem.*, **6,** 71 (1964). [d] Reference 19, p 92. [e] H. Siebert, *Z. Anorg. Allgem. Chem.*, **298,** 51 (1958). [f] B. O. Field and C. J. Hardy, *Quart. Rev.* (London), **18,** 361 (1964). [g] D. Brown and P. J. Jones, *J. Chem. Soc.*, *A*, 733 (1966). [h] C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **89,** 3066 (1967). [i] F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5,** 1128 (1966). [j] L. Sacconi, I. Bertini, and R. Morassi, *ibid.*, **6,** 1548 (1967). [k] J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **10,** 319 (1959). [l] D. K. Straub, R. S. Drago, and J. T. Donoghue, *Inorg. Chem.*, **1,** 848 (1962). [m] R. J. Fereday and D. Sutton, *Chem. Commun.*, 510 (1966). [n] C. D. Garner, D. Sutton, and S. C. Wallwork, *J. Chem. Soc.*, *A*, 1949 (1967). [o] C. C. Addison, D. W. Amos, D. Sutton, and W. H. H. Hoyle, *ibid.*, *A*, 808 (1967). [p] R. J. Fereday, N. Logan, and D. Sutton, *Chem. Commun.*, 271 (1968). [q] D. G. Karraker, *Inorg. Nucl. Chem. Letters*, **4,** 309 (1968). [r] R. P. Oertel and R. A. Plane, *Inorg. Chem.*, **7,** 1192 (1968). [s] This work. [t] Sometimes two or more bands are reported in this region.

ever, this band is usually weak, and any proposed structures should be corroborated by the positions of the C–N stretch, ν(CN), the N–C–S bend, δ(NCS), and the metal–ligand stretch. Foster and Goodgame[23] have shown that in six-coordinate isothiocyanato complexes the metal–nitrogen stretch occurs at a frequency about 20 K higher than the metal–chlorine stretch of the analogous chloro complexes. Metal–sulfur stretches of thiocyanato complexes tend to be weak and of lower energy, somewhat above the metal–bromine stretches.

After the diarsine bands have been deleted, the infrared spectrum of the thiocyanate salt consists of the bands reported in Table VI. The assignments for the ionic thiocyanate were inferred from the intensities. The bands at 2086, 827, and 467 K are indicative of an isothiocyanato group, especially in view of the results of Cunninghame, Nyholm, and Tobe[24] for $CoCH_3As(o\text{-}C_6H_4As(CH_3)_2)_2(NCS)_3$ (see Table VI). If the assignment of 324 K for the Co–Cl stretch is correct,[25] 338 K is a very reasonable value for a Co–N stretch.

Dinitrato Complex.—This complex forms in an aqueous 2 *N* nitric acid solution. The infrared spectrum shows no indication of water, either bound or lattice. The bands which are observed are typical of bound nitrato groups (see Table VII), but, in the absence of Raman data, no conclusions as to the mode of bonding can be drawn. The pmr spectrum contains four methyl resonances, indicating a *cis* structure.

Oxalato Complex.—The method of preparation of this complex was similar to that used for the carbonato complex. Only with the hexafluorophosphate anion was a monomeric cation precipitated. The pmr spectrum is very nearly identical with that of $[Co(diars)_2CO_3]PF_6$ and indicates a *cis* complex. The infrared spectrum, after deletion of diarsine and PF_6^- bands, is reported in Table VIII. These values correspond rather well to the ranges reported in Table VIII for

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(23) D. Foster and D. M. L. Goodgame, *Inorg. Chem.*, **4,** 715 (1965).

(24) R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 5800 (1964).

(25) The assignment of the metal–ligand vibrations is discussed in B. K. W. Baylis, "A Simple Triatomic Model for Calculating Metal–Ligand Vibrations," in "Coordination Chemistry—Papers Presented in Honor of Professor John C. Bailar, Jr.," S. Kirschner, Ed., Plenum Press, New York, N. Y., 1969, p 311.

TABLE VIII
INFRARED SPECTRA OF THE OXALATE GROUP

Compounds	Band freq, K					Ref
$O_2C_2O_2^{2-}$	1640 s	1420 w, 1335 s	1316 s		780, 774 s	*a*
$MO_2C_2O_2$	1722–1632 s 1700–1610 s[g]	1433–1387 s	1305–1228 m–s	914–855 w–m	825–775 w–s[g]	*a–e*
$MO_2C_2O_2M$	1660–1637 s 1657–1630 s	1367–1344 w	1325–1293 m	885–880 w	802–783 m–s	*a, d*
Bridging unidentate	1567–1562 s	1365–1351 s	1310–1300 s		760–740 s	*d*
cis-CoD_2ox^+	1708 s 1680 s	1356 s			774 m	*f*

[a] N. F. Curtis, *J. Chem. Soc.*, 4109 (1963). [b] J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36,** 324 (1962). [c] H. Siebert, *Z. Anorg. Allgem. Chem.*, **298,** 51 (1958). [d] N. F. Curtis, *J. Chem. Soc., A*, 1584 (1968). [e] Reference 19, pp 211–213. [f] This work. [g] Sometimes two bands are reported in this region.

bidentate oxalato complexes, except that no band is observed in the region 1305–1228 K. It is possible that hydrogen-bonding effects are present here as they are in the carbonato complexes, for a strong band at 1210 K was observed in a sample which had not been dried thoroughly and showed ν(OH) bands due to water.

Summary

(1) Proton magnetic resonance spectra can be used to determine whether a bis-diarsine complex is *cis* or *trans:* spectra of the *cis* complexes contain four methyl resonances whereas those of *trans* complexes contain only one.

(2) The methyl-rocking region (920–840 K) of the infrared spectra can also be used if the samples are quite pure and especially if both isomers are at hand: the *cis* isomers show more bands in this region than do the *trans* isomers.

(3) It is generally possible to prepare *cis* diarsine complexes from *trans*-dihalo starting materials if silver salts are used to precipitate the leaving halo groups.

(4) The following new complexes were prepared and characterized: *cis*-$[Co(diars)_2(OAc)_2]BF_4$, *cis*-$[Co(diars)_2CO_3]PF_6$, *cis*-$[(Co(diars)_2HCO_3)_2HCO_3](BF_4)_3$, *cis*-$[(Co(diars)_2HCO_3)_2HCO_3](ClO_4)_3$, *cis*-$[Co(diars)_2(NO_3)_2]ClO_4$, and *cis*-$[(Co(diars)_2ox]PF_6$. The following complexes which had originally been prepared by Nyholm and his coworkers were shown to be *trans:* *trans*-$[Co(diars)_2I_2]I$, *trans*-$[Co(diars)_2(OAc)_2]ClO_4$, and *trans*-$[Co(diars)_2(NCS)_2]NCS$. The nature of the metal–ligand bond was determined for the latter two.

(5) The bis(diarsine)cobalt(III) complexes which formed with the hard bases (OAc, NO_3, ox, CO_3) are quite similar to their bis-ethylenediamine analogs. Various differences, such as a tendency to form dimers and to react more slowly, can be explained by the use of nonaqueous solvents, by the absence of acidic hydrogens, and by consideration of steric effects. Thus no striking softening of the Co(III) ion by the soft diarsine ligand was observed. This finding is in agreement with that of Feltham and Silverthorn,[8] who observed no Co–As π-bonding effects in the visible spectra of some bis(diarsine)cobalt(III) complexes.

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