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Dissymmetric Arsine Complexes. Separation of the Racemic and Meso Isomers of Linear Quadridentate Arsines via Their Metal Complexes

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Two linear quadridentate tetra(tertiary arsines) have been prepared, one with three *o*-phenylene linkages (qars) and the other with a central *o*-phenylene linkage and two terminal trimethylene arms (fars). The racemic and meso forms of both arsines have been separated and identified via their cobalt(III) complexes. All of the thermodynamically accessible isomers of the dichloro complexes of both ligands have been isolated and identified and their topological equilibria investigated.

Linear quadridentate tetra(tertiary arsine) and phosphine ligands potentially provide systems where the topology and chirality of their metal complexes can be "tuned" to particular stereochemical demands, such as those required for metal-assisted asymmetric syntheses. The usual methods for preparing these ligands inevitably lead to the production of both meso and racemic forms, usually in similar proportions. Attempts at separating these isomers and resolving the (optically stable) racemic form by conventional methods are made difficult by their unattractive physical properties. It has become apparent recently,[1,2] however, that when these ligands are complexed to a suitable metal, their complexes provide tractable derivatives which are readily susceptible to conventional techniques.

In a recent paper[2] we described how these procedures could be applied to the arsine ligand tetars (Figure 1) and suggested that these were generally applicable. This claim is supported here where we describe the separation of the meso and racemic forms of two analogous quadridentate arsines qars and fars (Figure 1) via their cobalt (III) complexes. In addition, the factors which may be involved in the topological equilibria of their complexes are discussed.

1. Separation of the Ligands and Topological Isomers

When a mixture of the racemic and meso forms of either the fars or qars ligand is allowed to react with a metal ion to form an octahedral metal complex, in principle, five topological isomers may be formed. The racemic ligands may adopt the cis-α, cis-β, and trans topologies, while only the cis-β and trans isomers can exist for the meso ligands (Figure 2). The cis-α topology with the meso ligands is excluded because of the stable geometry of the inner arsenic atoms which act as constraints to the terminal chelate arms.[2] It is thus possible to identify unambiguously complexes containing the racemic and meso ligands, provided the cis-α isomer is isolated and it is shown that there exist two independent sets of topological equilibria, of which one includes the cis-α isomer. This is most readily achieved with the cobalt(III) complexes of the arsines.

Figure 3 outlines the scheme for the preparation of the two arsines. The products in both cases were not distillable, and after the low-boiling fractions were removed, both ligand mixtures set as waxy solids.

We found that the most direct way of separating the isomers of the fars ligand was via the $[Co(fars)Br_2]Br$ derivatives which, unlike the dichloro analogs, exist only as the cis-α isomer of the racemic ligand and the trans isomer of the meso ligand in water or methanol solutions. These were cleanly separated from methanol–acetone solutions by the addition of ether. The qars ligand is more restrictive in the topologies it will adopt and the violet *cis*-α-$[Co(R,R{:}S,S\text{-qars})Cl_2]Cl$ and the green *trans*-$[Co(R,S\text{-qars})Cl_2]Cl$ isomers of the racemic and meso ligands, respectively, are easily separated by precipitation from water solutions.

Conversion of the *cis*-α-$[Co(R,R{:}S,S\text{-fars})Br_2]^+$ ion to $[Co(R,R{:}S,S\text{-fars})Cl_2]^+$ in aqueous HCl leads to the formation of the violet *cis*-α-, the violet-brown *cis*-β-, and the green *trans*-$[Co(R,R{:}S,S\text{-fars})Cl_2]^+$ ions. All three were isolated pure as their perchlorate salts. A similar conversion of the *trans*-$[Co(R,S\text{-fars})Br_2]^+$ ion gives a mixture of the *cis*-β- and *trans*-$[Co(R,S\text{-fars})Cl_2]^+$ isomers, of which the latter is easily isolated from the reaction mixture, while the former is conveniently prepared from the *cis*-β-$[Co(R,S\text{-fars})CO_3]^+$ complex by the action of HCl. Apart from the *cis*-α-$[Co(R,R{:}S,S\text{-qars})Cl_2]^+$ and *trans*-$[Co(R,S\text{-qars})Cl_2]^+$ ions isolated from the initial separation of the ligands, the only other isomer isolated (or detected) for the dichloro complexes of the qars ligand was the *cis*-β-$[Co(R,S\text{-qars})Cl_2]ClO_4$ complex. Thus all the thermodynamically accessible dichloro isomers of the four ligands have been isolated. The structural assignments are confirmed by their NMR and visible absorption spectra.

2. Structural Assignments

Simple symmetry arguments show that the cis-α isomers of the racemic fars and qars ligands and the trans isomers of the racemic and meso ligands should have three environmentally different arsenic methyl groups. The only qualification to these assertions would arise if a number of conformational isomers existed for the terminal chelate rings of the fars ligands, but as we have shown elsewhere,[2] conformational equilibria of this kind, if they exist, are rapid at 30°. The cis-β isomers of any of the ligands have six environmentally different methyl groups. Thus the NMR spectra of the methyl proton resonances can distinguish the cis-β isomers. The *trans*-dichloro isomers are unambiguously distinguished from cis-α or cis-β isomers by their visible absorption spectra;

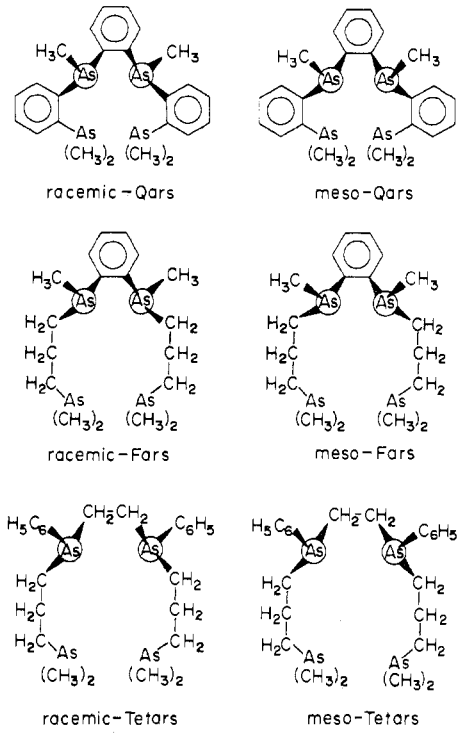

Figure 1. The structures of the three arsines.

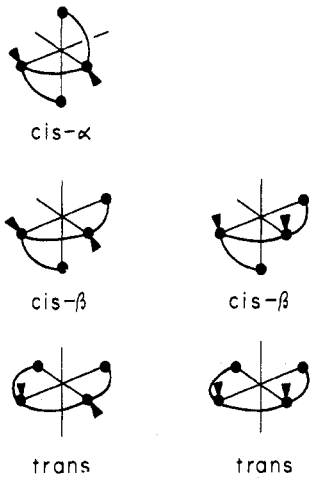

Figure 2. Possible topologies that the ligands can adopt. The wedges on the inner two donor atoms refer to the orientation of the third substituent on the arsenic atoms.

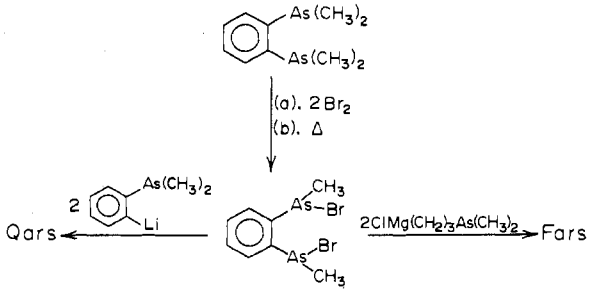

Figure 3. Outline of the methods employed for making the two arsines qars and fars.

the *trans*-dichloro isomers are always green.

Table I lists the relevant NMR data for these complexes. It will be seen that the expected patterns are observed. A feature of interest is the high-field shift of one of the methyl groups in the *cis*-β-[Co(*R*,*S*-qars)Cl_2]$^+$ ion. Molecular models suggest that one of the terminal methyl groups in this complex

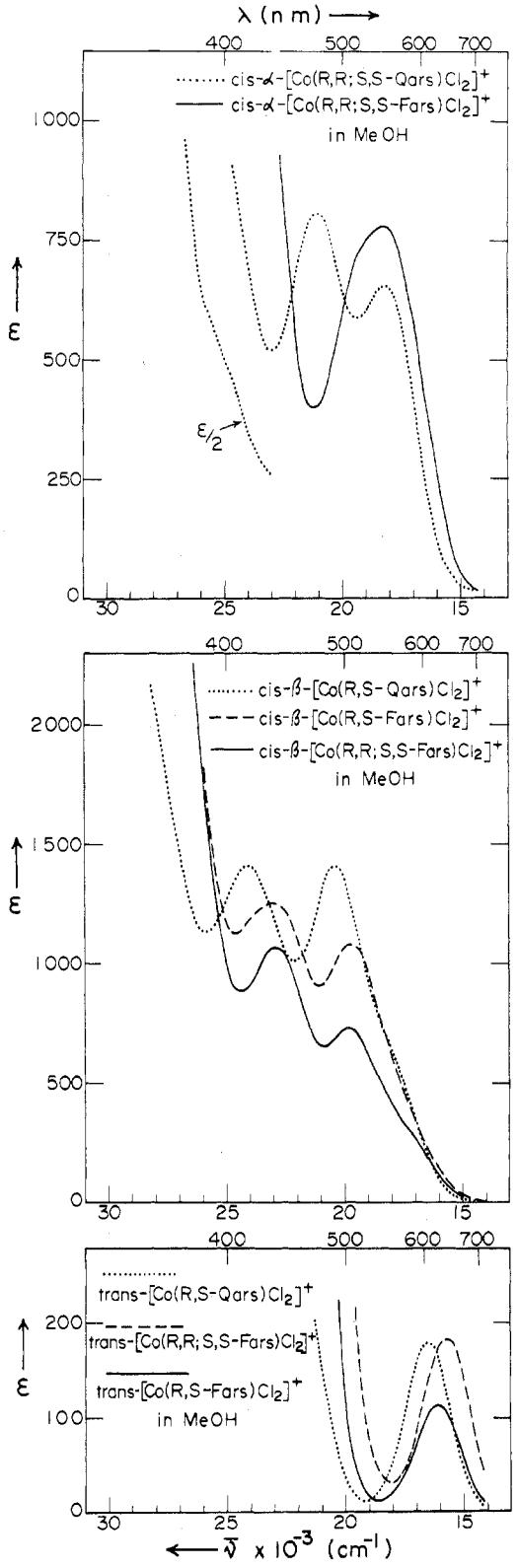

Figure 4. Visible absorption spectra of the various arsine complexes in different topologies. The spectra refer to dichlorocobalt(III) species.

is shielded by the two quasicoplanar benzene rings of the ligand. The amount of diamagnetic shielding, however, seems to depend critically on the amount of distortion in the system, which may account for the fact that the *cis*-β-[Co(*R*,*S*-qars)CO_3]$^+$ ion does not show such a drastic upfield shift. A similar shielding effect was observed for the complexed tetars ligands.[2,3]

Table I. NMR Data

Compd	As-CH_3, Hz	Solvent[b]
cis-α-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4	75, 97, 111	DMSO-d_6
	74, 98, 106	CD_3CN
cis-β-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4	87, 93, 102, 113,[c] 116	DMSO-d_6
	81, 93, 101, 104, 106, 116	CD_3CN
trans-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4	95,[c] 102	CD_3CN
	(159, 160.5, 171)	CD_3CN
cis-β-[Co(*R*,*S*-fars)CO_3]ClO_4	36, 86, 93,[c] 94, 102	CD_3CN
cis-β-[Co(*R*,*S*-fars)Cl_2]ClO_4	39, 80, 92, 99, 107, 109	DMSO-d_6
trans-[Co(*R*,*S*-fars)Cl_2]ClO_4	94, 97[c]	DMSO-d_6
	95, 98[c]	CD_2Cl_2
	(159.6, 165, 165.5)	CD_2Cl_2
cis-α-[Co(*R*,*R*:*S*,*S*-fars)Br_2]Br	82, 115, 122	$CDCl_3$
trans-[Co(*R*,*S*-fars)Br_2]Br	105, 107, 111	$CDCl_3$
cis-α-[Co(*R*,*R*:*S*,*S*-qars)Cl_2]Cl	116, 126, 135	DMSO-d_6
trans-[Co(*R*,*S*-qars)Cl_2]Cl	110, 122, 130	DMSO-d_6
cis-β-[Co(*R*,*S*-qars)CO_3]ClO_4	27, 107,[c] 114, 140, 142	CD_2Cl_2
cis-β-[Co(*R*,*S*-qars)Cl_2]ClO_4	−10, 97, 105, 127, 143, 155	CD_3CN

[a] At 60 MHz except the values in parentheses which were run at 100 MHz. [b] TMS as internal reference, 30°. [c] Intensity corresponds to two methyl proton resonances.

3. Absorption Spectra

Figure 4 shows the visible absorption spectra of the eight isomeric dichlorocobalt(III) complexes. The resolved absorption bands of moderate intensity are ascribed to "d–d" excitations. As is generally observed[2-5] for the *trans*-[Co(As)$_4$$Cl_2$]$^+$ chromophore, the *trans* complexes show bands of weaker intensity compared to those of the noncentric cis complexes. The resolved bands at around 16,000 cm^{-1} for the trans isomers are assigned to the $^1A_{1g} \rightarrow {}^1E_g$ transition derived from the $^1T_{1g}$ manifold; the other component is overlapped by the strong charge-transfer band.

The cis-β complexes also show a typical[2] d–d pattern for systems containing arsine ligands and are quite distinct from the spectra shown by similar cobalt(III) complexes containing "hard" donor atoms such as nitrogen and oxygen. The lower energy peaks around 20,000 cm^{-1} are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions, and it will be noted that, to lower energies, these absorptions show evidence of splitting, as is expected, because of the C_{2v} field. All three cis-β complexes, however, show another clearly resolved band in the region 23,000–24,000 cm^{-1}. Recognizing that the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the $[Co(As)_6]^{3+}$ chromophore occurs[5] at 23,000 cm^{-1}, these higher energy bands cannot be components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the *cis*-[Co(As)$_4$$Cl_2$]$^+$ chromophore since the weaker field chloro ligands should displace all of the $^1A_{1g} \rightarrow {}^1T_{1g}$ components to lower energies. We therefore assign these bands to components of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. If this is so, then the effect of the arsenic donor atoms is to reduce drastically the free-ion interelectronic repulsion parameters of the central cobalt atom. This suggests that the cobalt d orbitals have expanded by bonding to the arsenic atoms.

The d–d spectra of the cis-α complexes are more difficult to interpret but it is clear that the bands at 18,500 cm^{-1} for both complexes represent components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. One of the complexes shows a resolved higher energy band at 21,000 cm^{-1}; the other does not. Since this band is displaced about 2000 cm^{-1} to lower energies compared to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the $[Co(As)_6]^{3+}$ chromophore, it is possible to assign it to the other $^1A_{1g} \rightarrow {}^1T_{1g}$ component, although the reduced interelectronic repulsions in these complexes could lead to overlap, in this region, with components derived from the $^1A_{1g} \rightarrow {}^1T_{2g}$ manifold.

Table II

Compd	Solvent[a]	Isomer equilibrium % Cis-α	Cis-β	Trans
[Co(*R*,*R*:*S*,*S*-fars)Cl_2]$^+$	1 *M* HCl	60	40	0
	CH_3OH	20	20	60
[Co(*R*,*S*-fars)Cl_2]$^+$	1 *M* HCl		15	85
	CH_3OH		0	100
[Co(*R*,*R*:*S*,*S*-qars)Cl_2]$^+$	1 *M* HCl	100	0	0
	CH_3OH	100	0	0
[Co(*R*,*S*-qars)Cl_2]$^+$	1 *M* HCl		30	70
	CH_3OH		0	100
[Co(*R*,*R*:*S*,*S*-tetars)Cl_2]$^+$	1 *M* HCl	80	20	0
	CH_3OH	75	5	20
	CH_3CN	85	15	0
[Co(*R*,*S*-tetars)Cl_2]$^+$	1 *M* HCl		0	100
	CH_3OH		0	100
	CH_3CN		0	100

[a] All isomer proportions refer to the boiling temperature of the solvents.

4. Topological Equilibria

The topological equilibria of the dichlorocobalt(III) complexes of the two ligands were measured in 1 *M* HCl and in methanol solutions. The results are collected in Table II, together with similar data for the tetars complexes for comparison. These equilibria were measured for about 10^{-3} *M* solutions and, unlike the case for the corresponding aminecobalt(III) complexes, there is very little solvolysis of the chloro groups in aqueous solutions. In fact, the complexes exist as the dichloro species to the extent of at least 98% under the conditions used, and hence the values in the table are uncomplicated by solvolysis. The same equilibria are obtained starting with any given isomer of a topological set and, in all cases, the geometry of the inner arsenic atoms is preserved.

The difference in topological equilibria for the [Co(*R*,*R*:*S*,*S*-qars)Cl_2]$^+$ ion compared to those of the [Co(*R*,*R*:*S*,*S*-fars)Cl_2]$^+$ and [Co(*R*,*R*:*S*,*S*-tetars)Cl_2]$^+$ ions is quite striking in that the all-phenyl-linked ligand retains its cis-α geometry under all conditions tried, whereas the other two, with their terminal six-membered chelate rings, are flexible in the topologies they adopt. A consideration of scale molecular models tends to confirm these observations in that there appear to be no gross steric impediments to the racemic tetars and fars ligands adopting any of the cis-α, cis-β, or trans topologies, but the racemic qars ligand appears to experience severe strain in forming any topology other than cis-α. Molecular models are less reliable in suggesting the preferred topologies of the meso ligands. Thus, the meso tetars and meso fars ligands appear to be devoid of strain or serious nonbonding interactions in either the cis-β or trans topology, but, contrary to observation, molecular models suggest that the cis-β geometry of the meso qars ligand is the less strained.

Some time ago we pointed to some of the characteristics required in designing multidentate ligands to achieve particular topologies.[6,7] These considerations are still useful, although they have been superseded, on a case by case basis, by the more precise techniques employed by conformational energy minimization calculations.[8,9] Our recent observations[2,3,10,11] on the topologies of cobalt(III)–arsine complexes, however, indicate additional topologically determining factors, some of which appear to originate in the nature of the metal–ligand bonds. We briefly mention some of these.

For the racemic tetars ligand, the introduction of a bidentate chelate with a small "bite", as in the cases of the CO_3^{2-}, SO_4^{2-}, and O_2^{2-} ligands, induces the complexes to adopt the cis-β geometry almost exclusively.[3,12] A single-crystal X-ray structure of the "sideways" bonded peroxocobalt(III)[12] complex *cis*-[Co(*R*,*R*-tetars)O_2]ClO_4 shows that the two

arsenic donor atoms trans to the CoO_2 bonds move toward the dioxygen moiety so that the trans $CoAs_2$ angle is almost 110°.[13] In fact, the system resembles a trigonal bipyramid. Whatever the reasons for this, it is clear that a cis-α geometry would not allow for an expansion of the trans $CoAs_2$ angle because, in this geometry, this angle is held by a five-membered ring which is unlikely to allow angles greater than 90°. If it is assumed that the other small "bite" ligands also require an expanded trans $CoAs_2$ angle, then their preference for the cis-β topologies can be understood. The reverse condition may also hold in that, if two substituents expand an octahedral angle, then these substituents may tend to lie opposite a $CoAs_2$ angle which can contract most easily. This may be the reason that the two complexes $[Co(R,R:S,S\text{-tetars})Br_2]^+$ [3] and $[Co(R,R:S,S\text{-fars})Br_2]^+$, with two large cis bromide ligands which might force an expansion of the $CoBr_2$ angle, are stable exclusively as cis-α, rather than cis-β, in all common solvents. This, of course, does not explain why trans complexes are not formed.

Another factor, apparently electronic in origin, has been observed for the $[Co(diars)_2X_2]^+$ systems[10,11] (diars = *o*-phenylenebis(dimethylarsine)). When X is a weak- or medium-field *negatively charged* ligand, the complexes are exclusively trans at equilibrium in common solvents. However, if the X ligands impress a very strong field, in fact stronger than As, then cis complexes exist at equilibrium. Thus $[Co(diars)_2X_2]^+$ systems, where $X^- = H^-$, CN^-, and CH_3^-, all have sizable amounts of cis complexes at equilibrium; the H^- ligand with the strongest field of all has 90% *cis*-$[Co(diars)_2(H)_2]^+$ in DMF at 30°.[10] We suppose that to some extent this is related to the strong cobalt–ligand bonds that are formed in these complexes. It is possible that, since in the trans topology the two X ligands share the same orbitals for bonding whereas in the cis geometry this can be avoided to some extent, the strong-field ligands can bond more effectively in the cis configuration than in the trans. Some experimental support is given to this by the fact that the H^- ligand has a strong trans-labilizing influence in these complexes.[10]

These types of effects have been generally ignored in conformational calculations which have proved successful in systems where gross distortions are absent and where the donor atoms have similar ligand fields. It is not easy to include these effects in such calculations but the topological equilibria for the $[Co(R,R:S,S\text{-fars})Cl_2]^+$ ions and the more extensive series described[3] for the $[Co(R,R:S,S\text{-tetars})X_2]^+$ systems may be governed by electronic factors, at least to some extent. For example, it is not obvious why for the racemic tetars ligand the dichloro complex gives all three isomers, the dibromo complex only gives cis-α, the dinitro complex is nearly all trans at equilibrium, and the dicyano complex gives 60% trans, 40% cis-α, and no detectable amounts of cis-β whereas the diisothiocyanato and diazido complexes give substantial proportions of cis-β.[3] We think electronic factors related to the Co–X bond play some part in determining the topological outcome.

5. Experimental Section

(a) Preparation of the fars Ligands. *o*-Phenylenebis(methylbromoarsine). A solution of *o*-phenylenebis(dimethylarsine)[14,15] (10 g) in dry (P_2O_5) carbon tetrachloride (80 ml) was placed under nitrogen in a 500-ml, three-necked flask, fitted with an efficient magnetic stirrer and a reflux condenser. Bromine (11.6 g, 10% excess) in dry carbon tetrachloride (100 ml) was added dropwise to the well-stirred, warm (~50°) solution of the diarsine. An off-white solid was immediately formed, and after all the bromine had been added, the mixture was refluxed for 0.5 hr. The solvent was then removed and the residue was heated to 130° and sucked at water pump pressure for 2 hr. The solid slowly transformed into an amber liquid as methyl bromide was given off. On cooling, the liquid solidified. [*Caution!* The solid is a powerful *vesicant* and produces painful, slowly healing blisters upon contact with skin. Gloves should be worn when handling the material.]

The yellow solid was extracted with hot, dry carbon tetrachloride (two 500-ml portions) and the solution was filtered. After removal of the solvent, the solid residue was distilled (twice) under high vacuum. It came over at 158–160° (0.5 mm) as a yellow oil which readily solidified as hexagonal plates (yield 80%). Anal. Calcd for $C_8H_{10}As_2Br_2$: C, 23.1; H, 2.4; Br, 38.4. Found: C, 22.8; H, 1.8; Br, 38.9.

***o*-Phenylenebis(dimethylarseno-γ-propylmethylarsine) (fars).** Magnesium (10.33 g, Anachemia) was placed under nitrogen, in a 2-l., three-necked flask, equipped with an efficient magnetic stirrer, reflux condenser, and a dropping funnel which contained γ-chloropropyldimethylarsine[16,17] (77.6 g) in dry ($LiAlH_4$) ether (50 ml). The reaction is difficult to initiate and the following procedure is reliable. The magnesium was covered with ether (25 ml) and methyl iodide (1 ml) was added. As soon as this reaction began, 10 ml of the ether solution containing the γ-chloropropyldimethylarsine was added. Within a few minutes a vigorous reaction set in and the rest of the arsine was added at such a rate as to maintain a continuously refluxing solution. After the addition was complete, the solution was heated and refluxed for 0.5 hr. The mixture was then cooled (acetone–ice) and ether (450 ml) was added.

To the resulting solution was slowly added *o*-phenylenebis(methylbromoarsine) (34 g) in warm, dry ($LiAlH_4$) benzene (100 ml) with vigorous stirring. The reaction is exothermic and was moderated by the rate of addition which was complete after 0.5 hr. The mixture was refluxed for 0.5 hr during which time a thick paste formed. It was cooled and carefully (*caution!*) hydrolyzed with NH_4Cl (30 g in 300 ml of deoxygenated water) followed by HCl (50 ml, 6 *N*). Two layers formed. The organic phase was separated and the aqueous phase was extracted with ether (two 100-ml portions). The organic solutions were combined, dried ($MgSO_4$), and filtered, and the solvent was removed under reduced pressure. The resulting yellow oil was heated to 200° and pumped under high vacuum to remove volatile materials. The crude fars ligand remained (43 g).

(b) Separation of the Racemic and Meso fars Ligands. *cis*-α- and *trans*-$[Co(fars)Br_2]Br$. The crude fars ligands (6.3 g) in ether (50 ml) were filtered, under nitrogen, into a solution of cobalt acetate tetrahydrate (2.9 g) in methanol (100 ml). Air was drawn through the deep reddish solution for 2 hr, whereafter HBr (4 ml, 8.5 *M*) was added and the now brown solution was aerated for a further 18 hr. The solvent was removed and the dark gummy residue was taken up in hot water (175 ml) and was boiled for 5 min. After HBr (2.2 ml, 8.5 *M*) was added, the solution was cooled and extracted with methylene chloride (ten 100-ml portions). The red aqueous layer was discarded. The green extracts were dried ($MgSO_4$) and evaporated to dryness.

The residue was taken up in methanol (5 ml) and upon the addition of acetone (20 ml) crystals began to form. In order to remove the arsenic side products, ether (500 ml) was added and the resulting fine crystals were collected and washed thoroughly with ether (7.0 g).

***cis*-α-$[Co(R,R:S,S\text{-fars})Br_2]Br$.** The above solid (7.0 g) was dissolved in warm methanol (80 ml) and the solution was diluted with acetone (80 ml). Ether (360 ml) was slowly added to the solution which began to deposit deep green, almost black, crystals of the cis-α complex. The solution was cooled and allowed to stand at 0° for 24 hr, after which time the crystals (2.2 g) were collected and washed with acetone–ether (1:10), then with acetone (10 ml), and finally with ether.

The combined filtrate and washings were evaporated to dryness and the residue was taken up in methanol (15 ml) and then diluted with acetone (30 ml). More of the cis-α complex was obtained by the slow addition of ether (75 ml) and cooling at 0° for 24 hr. The crystals were collected and washed with acetone (10 ml) and then with ether. The filtrate and washings were set aside. These crystals (1.5 g) were recrystallized from methanol–acetone–ether (35:15:130 ml). The product (1.2 g) was combined with the first fraction (2.2 g) and recrystallized to give 3 g of pure *cis*-α-$[Co(R,R:S,S\text{-fars})Br_2]Br$ as deep green blocks. The filtrate was combined with that obtained from the first fractionation. Anal. Calcd for $[Co(C_{18}H_{34}As_4)Br_2]Br$: C, 25.5; H, 4.0; As, 35.3; Br, 28.2; Co, 6.9. Found: C, 25.4; H, 4.1; As, 35.3; Br, 27.9; Co, 6.9.

***trans*-$[Co(R,S\text{-fars})Br_2]Br$.** The solvent was removed from the combined filtrates obtained after the isolation of the cis-α complex. The residue was taken up in boiling water (200 ml) and the solution

was filtered. To the hot solution was added, dropwise, HBr (1 ml, 4.5 *M*). On cooling, the solution began to deposit green crystals as well as a brown oil, and after it was allowed to stand at 0° for 7 days, the crystals were collected. These were dissolved in hot water (175 ml) and reprecipitated by the dropwise addition of HBr (1 ml, 4.5 *M*). After the mixture was allowed to stand at 25° for 24 hr, the green crystals were collected and dried in an oven at 100°. One crystallization from ethanol (60 ml) by the slow addition of ether (60 ml) gave the pure trans compound (1.7 g) as deep brown-green needles which slowly transformed to brown crystals after remaining at 100° for 24 hr. The latter were analyzed. Anal. Calcd for [Co($C_{18}H_{34}As_4$)Br_2]Br: C, 25.5; H, 4.0; Br, 28.2. Found: C, 25.5; H, 4.0; Br, 27.7.

(c) Preparation and Separation of *cis*-α-, *cis*-β-, and *trans*-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4. *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Br_2]Br (2.0 g) was dissolved in HCl (30 ml, 5 *M*) and boiled for 5 min, whereafter the solution became purple-brown.

***trans*-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4.** After dilution of the cool solution with water (30 ml), the green trans isomer was extracted into methylene chloride (three 20-ml portions). The combined extracts were then shaken with water (three 30-ml portions) to remove the small amount of cis-α and cis-β isomers which extract from concentrated solutions. The green methylene chloride extracts were dried and pumped to dryness. The greenish brown residue was taken up in a minimum amount of acetone and the trans complex was precipitated by adding $NaClO_4$ (2 g) in water (100 ml). After the mixture was allowed to stand for 1 hr, the green crystals were collected and washed with water, then with 10% acetone–ether, and finally with ether. It was twice recrystallized from acetone (10 ml) by the slow addition of ether. The pure compound deposited as green feather-like crystals (0.05 g); Λ_M = 130 ohm^{-1} cm^2 mol^{-1} (5.7 × 10^{-4} *M* in CH_3CN at 25°). Anal. Calcd for [Co($C_{18}H_{34}As_4$)Cl_2]ClO_4: C, 27.7; H, 4.4; Cl, 13.7. Found: C, 27.7; H, 4.2; Cl, 13.2.

***cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4.** To the combined aqueous phases obtained after the extraction of the trans isomer was added $NaClO_4$ (2 g) in water (50 ml), which caused immediate precipitation of the cis-α and cis-β isomers as a deep red powder. The mixture was extracted with methylene chloride (four 50-ml portions), and after drying ($MgSO_4$) of the extracts, the solvent was removed to give a purple, almost black, residue consisting of the cis-α (75%) and cis-β (25%) isomers.

The residue was quickly taken up in chloroform (20 ml) and the mixture allowed to stand for 12 hr at 25°. The purple crystals of the cis-α isomer were collected and washed with a little chloroform and then with ether. The filtrate was set aside.

The solid was recrystallized from acetonitrile (10 ml) by the slow addition of ether (80 ml). After the solution was allowed to stand at 0° for 12 hr, the feathery needles of the pure cis-α isomer were collected. It crystallizes with 0.5 mol of ether (confirmed by NMR) which was removed by heating the compound at 130° for 24 hr (0.8 g); Λ_M = 129 ohm^{-1} cm^2 mol^{-1} (3.78 × 10^{-4} *M* in CH_3CN at 25°). Anal. Calcd for [Co($C_{18}H_{34}As_4$)Cl_2]ClO_4: C, 27.7; H, 4.4; As, 38.5; Cl, 13.7; O, 8.2; Co, 7.6. Found: C, 27.7; H, 4.6; As, 38.0; Cl, 13.8; O, 8.6; Co, 7.3.

***cis*-β-[Co(*R*,*R*:*S*,*S*-fars)Cl_2]ClO_4.** The chloroform filtrate consists mainly of the cis-β isomer. After removal of the chloroform under vacuum, the residue was taken up in acetone (3 ml), diluted with ethanol (30 ml), and filtered. The filtrate was allowed to stand at 0° for 0.5 hr whereupon the cis-β isomer began to deposit as purple-brown blocks. Further precipitation was induced by the addition of ether (60 ml) over a period of 12 hr to the solution at 0°. The cis-β isomer was collected and recrystallized from acetonitrile (10 ml) by slowly adding ether (50 ml). The pure compound deposits as purple-brown blocks (0.2 g); Λ_M = 131 ohm^{-1} cm^2 mol^{-1} (3.65 × 10^{-4} *M* in CH_3CN at 25°). Anal. Calcd for [Co($C_{18}H_{34}As_4$)-Cl_2]ClO_4: C, 27.7; H, 4.4; Cl, 13.7. Found: C, 27.9; H, 4.3; Cl, 13.8.

(d) Preparation of the *trans*- and *cis*-β-[Co(*R*,*S*-fars)Cl_2]$^+$ Isomers. ***trans*-[Co(*R*,*S*-fars)Cl_2]Cl·2H_2O·HCl.** *trans*-[Co(*R*,*S*-fars)Br_2]Br (1.0 g) was dissolved in hot water (50 ml) and to it was added HCl (50 ml, 12 *M*). The solution was boiled for 3 min and allowed to stand at 25° for 12 hr. The green feathery crystals which precipitated out of the brown (cis-β) solution were collected and washed with 5% acetone–ether and then with ether. The compound was recrystallized from warm water (20 ml) by adding HCl (20 ml; 12 *M*) (0.3 g). The product is acidic upon dissolution in water and crystallizes with HCl of crystallization. Anal. Calcd for [Co($C_{18}H_{34}As_4$)Cl_2]Cl·2H_2O·HCl: C, 27.4; H, 5.0; Cl, 18.0. Found: C, 27.3; H, 5.0; Cl, 17.3.

***trans*-[Co(*R*,*S*-fars)Cl_2]ClO_4.** The brown filtrate from above was brought to the boil and $HClO_4$ (2 ml, 12 *M*) was added. On cooling the green product which deposited was collected, taken up in acetonitrile (25 ml), and reprecipitated by the addition of $HClO_4$ (50 ml, 0.1 *M*). It was collected and washed with water, then with 10% acetone–ether, and finally with ether. It was recrystallized from acetonitrile (25 ml) by adding ether (75 ml) and deposited as green flakes (0.3 g). Λ_M = 134 ohm^{-1} cm^2 mol^{-1} (3.66 × 10^{-4} *M* in CH_3CN at 25°). Anal. Calcd for [Co($C_{18}H_{34}As_4$)Cl_2]ClO_4: C, 27.7; H, 4.4; Cl, 13.7. Found: C, 27.9; H, 4.5; Cl, 13.8.

***cis*-β-[Co(*R*,*S*-fars)CO_3]ClO_4·0.25$NaClO_4$.** To *trans*-[Co(*R*,*S*-fars)Br_2]Br (1 g) in methanol (5 ml) was added Na_2CO_3 (0.15 g) in water (5 ml). The resultant mixture was heated on a steam bath for 10 min to give a red-orange solution. After the addition of $NaClO_4$ (2 g) in water (20 ml), the volume was reduced to about 5 ml under reduced pressure, whereupon the red-orange product precipitated out. The crystals were collected and washed thoroughly with ether. They were crystallized twice from acetonitrile (40 ml) by slowly adding ether (40 ml). The compound deposited as dark red blocks which were homogeneous under the microscope (0.7 g). Anal. Calcd for [Co($C_{18}H_{34}As_4$)CO_3]ClO_4·0.25$NaClO_4$: C, 28.6; H, 4.3; Cl, 5.6. Found: C, 28.8; H, 4.6; Cl, 5.6.

***cis*-β-[Co(*R*,*S*-fars)Cl_2]ClO_4.** Cold HCl (2 ml, 12 *M*) was added to *cis*-β-[Co(*R*,*S*-fars)CO_3]ClO_4·0.25$NaClO_4$ (0.3 g). The mixture was shaken and kept at 10° until the evolution of CO_2 ceased (~5 min). Water (5 ml) containing 4 drops of concentrated $HClO_4$ was then added; the resulting dark brown solid was collected and washed with water and then ether. It was recrystallized from acetone (70 ml) by slowly adding ether (140 ml). The complex deposited as dark brown diamond-shaped crystals (0.2 g). Λ_M = 128 ohm^{-1} cm^2 mol^{-1} (4.17 × 10^{-4} *M* in CH_3CN at 25°). Anal. Calcd for [Co($C_{18}H_{34}As_4$)Cl_2]ClO_4: C, 27.7; H, 4.4; Cl, 13.7. Found: C, 27.8; H, 4.4; Cl, 13.7.

(e) Preparation of *o*-Phenylenebis(*o*-dimethylarsinophenylmethylarsine). *o*-Bromophenyldimethylarsine[18] (66 g) was prepared from *o*-bromophenyldichloroarsine[19] and was placed in a 3-l. three-necked flask, fitted with a 500-ml dropping funnel, condenser, and an efficient magnetic stirrer. Dry ($LiAlH_4$) ether (400 ml) was added, and the whole system was flushed with nitrogen and then cooled to 0°. A solution of *n*-butyllithium (120 ml, 1.90 *M*) was then slowly added through a serum cap by means of a calibrated syringe. The solution was stirred for a few minutes at 0° and then refluxed for 1 hr, after which the now cloudy solution was cooled to 0°. A solution of *o*-phenylenebis(methylbromoarsine) (35 g) in dry ($LiAlH_4$) benzene (250 ml) was then added to the well-stirred solution over a period of 1 hr. The turbid orange solution was refluxed for 15 min after which time it attained a clear, light orange color.

The mixture was cooled, stirred, and hydrolyzed with HCl (400 ml, 0.2 *N*). The organic phase was separated and the remaining aqueous phase extracted with ether (two 500-ml portions). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. After the residue was heated to 180° and pumped at 0.1 mm, the remaining product (qars) solidified into a wax at 25° (33 g).

(f) Separation of the Isomers of the qars Ligand. ***cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl_2]Cl·H_2O.** A solution of crude qars (23.5 g) in ether (150 ml) was filtered into a solution of cobalt acetate tetrahydrate (9.0 g) in methanol (500 ml) and the resulting deep brown solution was aerated for 3 hr. Then HCl (20 ml, 12 *M*) was added and the aeration was continued for a further 5 hr. The resulting solution was filtered and evaporated to dryness and the gummy residue dissolved in acetonitrile. Ether (1 l.) was added to the dark brown solution to deposit a deep brown oil and a greenish supernatant liquor which contained arsenic side products. The liquor was decanted off and the residue was dried and extracted with boiling water (three 500-ml portions). The cooled aqueous extracts were extracted with methylene chloride (three 300-ml portions), and after HCl (5 ml, 12 *M*) was added, they were extracted again (three 300-ml portions). The remaining aqueous phase was discarded and the methylene chloride extracts were dried ($MgSO_4$) and pumped to dryness.

The residue was slurried with acetonitrile (25 ml) whereupon deep brown-violet crystals of the cis-α complex formed. These were filtered and the green-brown filtrate was retained. The violet crystals were taken up in boiling water (200 ml) and the solution was left to

crystallize at 25° for 24 hr. The violet needles of the cis-α complex were collected, washed with cold water, and dried. It was finally recrystallized from methanol (25 ml), acetone (25 ml), and acetonitrile (20 ml) by the slow addition of ether (275 ml). The pure product (3.1 g) deposited as deep violet needles or flakes. Λ_M = 64 ohm^{-1} cm^2 mol^{-1} (5.93×10^{-4} *M* in methanol at 25°). Anal. Calcd for $[Co(C_{24}H_{30}As_4)Cl_2]Cl \cdot H_2O$: C, 35.9; H, 4.0; Cl, 13.3; As, 37.4; Co, 7.4. Found: C, 36.4; H, 4.1; Cl, 13.1; As, 37.0; Co, 7.3.

trans-**[Co(*R*,*S*-qars)Cl$_2$]Cl.** The acetonitrile filtrate derived from the initial isolation of the cis-α complex was evaporated to dryness. It was recrystallized three times from hot HCl (0.1 *M*) solution to give the green trans complex as green needles. It was finally purified by crystallization from methanol by the careful addition of ether (1.5 g). Λ_M = 63 ohm^{-1} cm^2 mol^{-1} (1.07×10^{-3} *M* in methanol at 25°). Anal. Calcd for $[Co(C_{24}H_{30}As_4)Cl_2]Cl$: C, 36.8; H, 3.9; Cl, 13.6; Co, 7.5. Found: C, 36.9; H, 4.1; Cl, 13.3; Co, 7.3.

cis-β-**[Co(*R*,*S*-qars)CO$_3$]ClO$_4$.** *trans*-[Co(*R*,*S*-qars)Cl$_2$]Cl (1 g) was dissolved in methanol (10 ml) and water (10 ml). Lithium carbonate (0.2 g) was then added and the solution was refluxed on a steam bath for 20 min to give a red solution. After filtration, $NaClO_4$ (2 g) in water (100 ml) was added and the solution was extracted with methylene chloride (five 20-ml portions). The organic solvent was dried and removed under vacuum to give a red solid. This was taken up in acetonitrile (10 ml) and methanol (5 ml) and the product was crystallized by the slow addition of ether (30 ml). The carbonato compound deposited as red needles (0.45 g). Anal. Calcd for $[Co(C_{24}H_{30}As_4)CO_3]ClO_4$: C, 35.9; H, 3.6; Cl, 4.2. Found: C, 35.9; H, 3.6; Cl, 4.2.

cis-β-**[Co(*R*,*S*-qars)Cl$_2$]ClO$_4$.** This compound was prepared by the method described for *cis*-β-[Co(*R*,*S*-fars)Cl$_2$]ClO$_4$ using *cis*-β-[Co(*R*,*S*-qars)CO$_3$]ClO$_4$ (0.3 g) as starting material. It was recrystallized from acetonitrile (15 ml) by slowly adding ether (45 ml). It deposited as dark brown blocks (0.2 g). Λ_M = 84 ohm^{-1} cm^2 mol^{-1} (4.73×10^{-4} *M* in methanol at 25°). Anal. Calcd for $[Co(C_{24}H_{30}As_4)Cl_2]ClO_4$: C, 34.0; H, 3.6; Cl, 12.6. Found: C, 34.0; H, 3.6; Cl, 12.6.

Topological Equilibria. The complexes (1.5×10^{-3} *M*) were refluxed for 24 hr in 1 *M* HCl. All the complexes after a certain time suddenly isomerized by a Co(II) electron-transfer reaction.[3] This may occur within 1 hr but all of the reactions consistently occurred within 24 hr. The solutions were cooled and extracted with CH_2Cl_2. After removal of the solvent under vacuum the homogeneous residue was analyzed by NMR using the integrated methyl peak heights. In all cases the NMR spectrum only represented the appropriate isomeric mixture of complexes. For the methanol solution equilibrations 1.5×10^{-3} *M* complex solutions were used and the solutions were refluxed for 50 hr. The methanol was taken off under vacuum, the residue was taken up in water, and the isomers were extracted and analyzed as before. All of the equilibrations generate a small amount of Co(II) which is effectively retained in the aqueous layer.

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Registry No. *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Cl$_2$]ClO$_4$, 56143-06-7; *cis*-β-[Co(*R*,*R*:*S*,*S*-fars)Cl$_2$]ClO$_4$, 55648-81-2; *trans*-[Co(*R*,*R*:*S*,*S*-fars)Cl$_2$]ClO$_4$, 55700-27-1; *cis*-β-[Co(*R*,*S*-fars)CO$_3$]ClO$_4$, 55648-79-8; *cis*-β-[Co(*R*,*S*-fars)Cl$_2$]ClO$_4$, 55700-29-3; *trans*-[Co(*R*,*S*-fars)Cl$_2$]ClO$_4$, 55700-31-7; *cis*-α-[Co(*R*,*R*:*S*,*S*-fars)Br$_2$]Br, 55648-82-3; *trans*-[Co(*R*,*S*-fars)Br$_2$]Br, 55721-18-1; *cis*-α-[Co(*R*,*R*:*S*,*S*-qars)Cl$_2$]Cl, 55648-83-4; *trans*-[Co(*R*,*S*-qars)Cl$_2$]Cl, 55700-32-8; *cis*-β-[Co(*R*,*S*-qars)CO$_3$]ClO$_4$, 55648-85-6; *cis*-β-[Co(*R*,*S*-qars)Cl$_2$]ClO$_4$, 55722-69-5; *trans*-[Co(*R*,*S*-fars)Cl$_2$]Cl·HCl, 55700-33-9; *o*-phenylenebis(dimethylarsine), 13246-32-7; *o*-phenylenebis(methylbromoarsine), 52120-03-3; γ-chloropropyldimethylarsine, 26900-75-4; *o*-phenylenebis(dimethylarsino-γ-propylmethylarsine), 55637-97-3; *o*-bromophenyldimethylarsine, 4457-88-9; *o*-phenylenebis(*o*-dimethylarsinophenylmethylarsine), 55637-98-4.

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Stereochemistry of Complexes of Multidentate Ligands. III.[1] Stereoselective Cobalt(III) Ion Complexes of 1,6-Bis(2(*S*)-pyrrolidyl)-2,5-diazahexane

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The synthesis of a new flexible tetraamine ligand, 1,6-bis(2(*S*)-pyrrolidyl)-2,5-diazahexane (*SS*-pyhn), is reported. Cobalt(III) complexes of *SS*-pyhn have been prepared and characterized. Only one isomer, Λ-*cis*-α-[Co(*SS*-pyhn)X$_2$]$^{n+}$ (X = Cl, H_2O, NO_2; X_2 = CO_3, Ox), was observed in the synthesis. The absolute configuration of this isomer is assigned on the basis of electronic absorption and CD spectra along with other chemical data.

Introduction

It has been observed that, when the cobalt(III) complexes of substituted derivatives of triethylenetetramine (trien) are synthesized, those flexible tetraamines which have asymmetric centers usually coordinate stereospecifically to the cobalt(III) ion. The absolute configurations of the complexes can be rationalized in terms of the positions of the substituents in the trien skeleton.[2-6]

The ligand prepared in this work, 1,6-bis(2(*S*)-pyrrolidyl)-2,5-diazahexane (*SS*-pyhn),[7] is expected to possess