tion values in both sets of experiments differ from the corresponding nitrosation reactions, the stereochemical studies in aqueous solution imply a common intermediate for nitrosation of *cis*-$[Co(en)_2ClN_3]^+$ and Hg^{2+}-catalyzed aquation of *cis*-$[Co(en)_2Cl_2]^+$ to $[Co(en)_2ClH_2O]^{2+}$.[16] It may be argued therefore that the competition differences arise from different ionic atmospheres for anion competition and selective solvation in the competition by neutral species. Clearly the charges in the transition states leading to the supposed intermediate are different, *e.g.*, $(H_3N)_5CoNNNNO^{3+}$ and $(H_3N)_5CoI{\cdot}Hg^{4+}$. However these problems are not involved for the stereochemical studies where common agreement is found. Additional evidence for selective solvation might be deduced from the slope of the competition plot for the NO^+ reactions in the CH_3CN-H_2O mixtures (Figure 4). Since this extrapolates to a nonzero intercept $[X_{\mathrm{CH_3CN}}] = 0$, the competition pattern must alter sharply at low CH_3CN concentrations. The monool also competes less effectively than the other reactions discussed. While these are not especially discriminating results, the competition is consistent with a predominantly dissociative path.

In the competition experiments in DMSO-water common results were also obtained for the nitrosations suggesting a common intermediate. Similarly, Hg^{2+}-catalyzed aquation of the halide complexes ($X^- = I^-, Br^-$) also gave a common result but now significantly more DMSO is incorporated than in the nitrosation experiments. Finally, the monool cleavage which now occurs by the acid-induced path gave results which are different from the others. Unlike the results in CH_3CN-H_2O solutions, the competition for DMSO appears to extrapolate in all cases to zero at [DMSO] = 0 although the apparently linear plot of mole fraction of DMSO in the solvent *vs.* mole fraction of competition product deviates at $X_{\mathrm{DMSO}} > 0.25$ (Figure 5) in the nitrosation and monool cases. This discontinuity correlates with discontinuities in other physical properties of DMSO-H_2O mixtures which imply specific solution aggregates.[17,18] Probably selective solvation of the intermediates is again involved although the results are insufficient at this time to substantiate this argument fully.

In short, no simple answer is obtained except that the competition by the neutral competitors in the nitrosation reactions is consistent with a common intermediate. On the whole the remaining results are consistent with the dissociative chemistry generally observed for substitution cobalt(III)-ammine complexes without giving strong support to this thesis. There is an additional implication that competition for $(H_3N)_5Co^{3+}$ and related species will be dependent on the charge of the immediate source of the intermediate and this aspect is being examined further.

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Registry No. $Co(NH_3)_5^{3+}$, 44236-77-3; $(NH_3)_5CoOHCo(NH_3)_5^{5+}$, 38467-75-3; $[(H_3N)_5CoOS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(H_3N)_5Co(OH_2)](ClO_4)_3$, 13820-81-0; DMSO, 67-68-5.

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Isomers of the Bis(diethylenetriamine)cobalt(III) Cation. Dependence of Equilibrium Isomer Proportions on Environmental Parameters

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The equilibrium distribution of the three geometric isomers of $[Co(dien)_2]^{3+}$ depends considerably on the environmental parameters solvation, ion association, and temperature. Addition of a basic oxy anion such as phosphate, selenite, or sulfate profoundly modifies the isomer distribution through the differential specific associations between the anion and the three isomers. The relative magnitudes of the specific interactions with phosphate as deduced from isomer proportions measurements are correlated with the measured association constants of the three isomers with that anion, and they are rationalized in terms of the detailed molecular structures of the isomers. The equilibrium isomer distribution measurements carried out at different temperatures lead to quantitative assessment of the enthalpy and entropy differences between the isomers. These thermodynamic data allow the first comparison of experimental equilibrium results with the predictions from energy-minimized conformational analysis calculations for different topological forms of a multidentate ligand complex and indicate the limitations of the present calculative methods.

Introduction

It has been appreciated for many years that a number of factors may determine the relative stabilities of the various isomeric forms of a metal complex, where these forms differ in relative geometry, *i.e.*, geometric isomers, internal diastereoisomers, or conformational isomers.[1] These factors include ion association, solvation, temperature, intramolecular nonbonded atomic interactions, and statistical weighting factors. The quantitative evaluation of all these factors, either on an experimental or on a theoretical basis, has not been possible however since it is recognized that they are not all independent. Even the relative importance of intramolecular and intermolecular factors is not generally known.

Experimentally, the reliable quantitative data for equilibrium distributions of isomers are essentially confined to some cobalt(III) complexes, with equilibrium frequently

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being established by the presence of charcoal.[2] Frequently the relative isomer proportions have been determined under only one particular set of experimental conditions of temperature, solvent, pH, and counterion concentration, and few studies of isomer proportions as functions of variations in these environmental parameters are apparent in the literature.[3-6]

We here report a more comprehensive experimental study of the influence of these environmental factors on the complex system $[Co(dien)_2]^{3+}$, dien = diethylenetriamine. This system is particularly useful for such a study. It is inert and free of possible complications such as disproportionation or hydrolysis or ligand substitution reactions which are inherent with complex systems involving mixed-ligand or acido substituents. The three geometric isomers[7] shown in Figure 1 have been well characterized,[8-10] and the effects of variations in environmental parameters are manifested primarily as changes in the geometric isomer proportions (rather than on conformer populations) so that the various effects can be measured quantitatively by chromatographic separations of the isomers from admixtures.[9]

Previous studies of this type on systems of noncoupled chelate rings such as $[Co(en)_3]^{3+}$ have demonstrated the effects of variations in temperature or ion association on conformer distributions. In noncoupled chelate ring systems equilibrium conformer proportions have to be deduced indirectly however from circular dichroism[3,11-15] or pmr[15-17] measurements, so that the data are semiquantitative only and interpretation is less certain.

The quantitative data obtained in the present study allow some conclusions as to the practical usefulness of present conformational analysis calculative methods for geometric isomers of metal complexes. Conformational analysis calculations have been refined in the present energy minimization techniques[4,18] to include all intramolecular factors. Such calculations yield enthalpy differences between isomers, as well as the "energy-minimized" detailed molecular

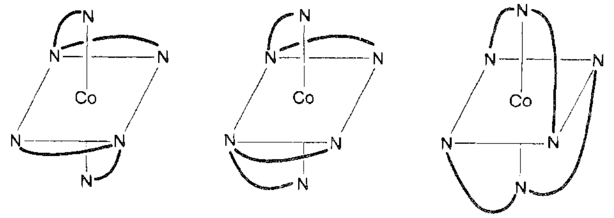

Figure 1. Topological isomers of $[Co(dien)_2]^{3+}$: left, *s-fac*; center, Δ-*u-fac*; right, *mer*.

structures for the isolated (hypothetical gas state) complex ions. The calculated strain energies are based on unknown energy zeros however, so that the applications to date have been restricted to comparisons of conformational isomers or internal diastereoisomers.[4] For these isomer types the intermolecular effects might be expected to be similar and the zero energies may reasonably be assumed approximately constant. The agreements between the energy-minimized isomer ratios (and structures) and the experimentally determined ratios (and structures) found for several systems so far have given some confidence in the calculations, so that for these systems at least it would seem that variations in entropy or intermolecular factors between the closely similar isomers are small.[6]

For geometric isomers the zero levels for the minimized energies need not be similar.[19] Some experimental isomer equilibrium data obtained earlier for the $[Co(dien)_2]^{3+}$ system allowed the first test of the calculative method for geometric isomers.[19] This comparison, of experimental $\Delta G°$ with calculated $\Delta H°$ values, involved unknown entropy and intermolecular factors however, so that the uncertainty as to zero-level imbalances in the comparison has remained.

The isomer equilibrium measurements on this complex system have been extended in the present paper so that the more useful comparisons of calculated and experimental $\Delta H°$ values between the isomers can now be made. The experimental results also allow some assessment of the contribution of environmental or intermolecular factors (ion-ion and ion-solvent interactions) and show that intermolecular factors are of considerable importance in determining the isomer distribution in $[Co(dien)_2]^{3+}$.

Experimental Section

Equilibrium proportions of the three geometric isomers of $[Co(dien)_2]^{3+}$ were determined from separate aerial oxidation procedures carried out under a variety of conditions. The reaction stoichiometry involved in all runs was

$$CoX_2 + 2dien + HX + {}^1/_4O_2 \xrightarrow{C} [Co(dien)_2]^{3+} + 3X^- + {}^1/_2H_2O$$

All aerations were of 36-hr duration and were carried out in the presence of charcoal, either at room temperature (18 ± 1°) or over a steam bath (80 ± 1°). Analytical grade reagents (Co(II) salts, added salts, solvents, and acids) and freshly distilled dien were used throughout. Freshly finely ground "BDH granulated charcoal for gas absorption" from the same batch was used, and its catalytic activity was tested to ensure that it satisfied the criterion of causing racemization of $(+)[Co(en)_3]^{3+}$ within 2 min at 90°.[20] The equilibrium preparations were carried out under a variety of conditions (Table I) which included variation in the anion X^-, variation of X^- concentration by adding salts in some runs, and variations in the cation concentration, temperature, solvent, and pH.

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Table I. Equilibrium Geometric Isomer Proportions in Aerial Oxidation Preparations of $[Co(dien)_2]^{3+}$ at 18° with Variations in Environmental Parameters

Solvent[a]	Co^{2+} anion	[Co], *M*	Added salt and [salt]	Isomer proportions, %		
				s-fac	*u-fac*	*mer*
Water	ClO_4^-	0.2, 0.02		8	30	62
Water	ClO_4^-	0.02	$NaClO_4$, 2 *M*	9	30	61
DMSO	ClO_4^-	0.01		6	14	80
DMA	ClO_4^-	0.005		7	14	79
DMA	ClO_4^-	0.005	$(Bu_4N)Cl$, 0.025 *M*	17	15	68
Water	NO_3^-	0.02		7	29	64
Water	NO_3^-	0.02	$NaNO_3$, 2 *M*	8	30	62
Water	CH_3COO^-	0.02		7	27	66
Water[b]	CH_3COO^-	0.02		14	42	44
Water	CH_3COO^-	0.02	$NaCH_3COO$, 2 *M*	12	31	57
Methanol	CH_3COO^-	0.02		18	29	53
t-C_4H_9OH	CH_3COO^-	0.02		20	45	35
Water	Br^-	0.4, 0.2, 0.02		7	28	65
Water	Br^-	0.2, 0.02	NaBr, 2 *M*	7	26	67
Water	Cl^-	0.4, 0.2, 0.02		7	28	65
Water[b]	Cl^-	0.02		12	41	47
Water	Cl^-	0.02	NaOH, 0.01 *M*; pH ~10	10	28	62
Water	Cl^-	0.2, 0.02	KCl, 2 *M*	7	28	65
Water	Cl^-	0.02	Na_2SeO_3, 2 *M*	59	28	13
Water	Cl^-	0.02	Phosphate buffer, 1 *M*; pH ~4	6	29	65
Water	Cl^-	0.02	Na_2HPO_4, 2 *M*	37	38	25
Water	Cl^-	0.02	Na_3PO_4, 0.01 *M*	16	31	53
Water	Cl^-	0.02	Na_3PO_4, 0.02 *M*	26	33	41
Water	Cl^-	0.02	Na_3PO_4, 0.04 *M*	37	33	30
Water	Cl^-	0.02	Na_3PO_4, 0.08 *M*	55	25	20
Water	Cl^-	0.02	Na_3PO_4, 0.4 *M* (satd)	59	29	12
Water	SO_4^{2-}	0.2, 0.02		19	34	47
Water[b]	SO_4^{2-}	0.02		22	44	34
Water	SO_4^{2-}	0.2, 0.02	K_2SO_4, 2 *M*	25	38	37

[a] DMSO = dimethyl sulfoxide, DMA = dimethylacetamide. [b] Temperature 80°.

Isomer Proportions in Aqueous Solution. The following procedure was typical of the runs in aqueous solution where anion was added in excess of that required by the reaction stoichiometry. $Co(NO_3)_2 \cdot 6H_2O$ (0.29 g, 0.0010 mol) was dissolved in water (30 ml) in a two-necked 100-ml round-bottom flask fitted with a reflux condenser to minimize evaporation during the aeration. To this solution $NaNO_3$ was added (8.5 g, 0.10 mol) and was dissolved as completely as possible before the addition of charcoal (2 g). A solution of dien (0.23 g, 0.0022 mol) and HNO_3 (1.1 ml of 1.0 *M*, 0.0011 mol) in water (20 ml) was then added. After aeration for 36 hr the charcoal was filtered off.

In the preparations involving phosphate or selenite ions the cobalt(II) salts of these anions were not used directly due to their low solubilities. Na_3PO_4 or Na_2SeO_3 was added to the solution of $CoCl_2$ as in the procedure above, and the aeration was carried out on the resulting suspension of the sparingly soluble cobalt(II) salt which precipitated along with some cobalt(II) hydroxide. This cobalt(II) salt dissolved as the reaction proceeded so that the preparation should have remained under equilibrium conditions throughout the process.

The filtrate from each preparation was diluted so that the concentration of the 1+ cations was less than 0.1 *M*, and aliquots (approximately one-fourth of the total volume) were applied to two columns (50 × 0.9 cm) of SP-Sephadex C-25 cation-exchange resin in the Na^+ form for duplicate isomer separations. The absorbed complex on each column was eluted with 0.3 *M* sodium (+)-tartrate solution to separate the isomers in the order *s-fac* (eluted first), *u-fac*, then *mer* (last).[9] The separated bands were collected and subsequently made up to standard volumes (25 or 50 ml) in volumetric flasks. The solutions were estimated either by cobalt atomic absorption or by spectrophotometry in 1- or 4-cm quartz cells. The optical densities of the eluted isomer bands from each chromatographic separation were measured at the first band maximum (*ca.* 466 nm)[9] on a manual Shimadzu QR-50 spectrophotometer against water reference, and it was established that each isolated isomer gave identical extinction coefficients in water and in 0.3 *M* sodium (+)-tartrate solution. The isomer proportion values given in Table I are the means from the duplicate separations for each run, and in separations where both analytical methods were used the analyses agreed. The percentage figures are each considered accurate to ±1.

Isomer Proportions in Nonaqueous Solvents. Modifications of the above procedure were necessary. For the runs in alcoholic solvents acetate counterion was used to confer solubility on the complex products. With the aprotic solvents, an aliquot of a dried (3-Å molecular sieves) 0.1 *M* solution of $Co(ClO_4)_2 \cdot 6H_2O$ in the appropriate solvent (dimethyl sulfoxide or dimethylacetamide), charcoal, and (if required) added anion as the tetrabutylammonium salt were mixed. dien and dien·$3HClO_4$ in 1.67 and 0.33 molar proportions compared to cobalt were added, and subsequent treatment was as above.

Determination of the Ion Association Constants between the Isomers of $[Co(dien)_2]^{3+}$ and PO_4^{3-}. Aliquots of Na_3PO_4 solution (2×10^{-2} *M*) were added to separate solutions of the geometric isomers of $[Co(dien)_2]^{3+}$ (*ca.* 2×10^{-3} *M*) in a stirred cell (3.2 cm) thermostated at 25.0° and containing a pH electrode assembly. The optical density at 300 nm was followed as a function of phosphate concentration using a Cary 16K spectrophotometer, and the pH was maintained at 11.5 by addition of NaOH using an ABU-1 autoburet. The ionic strength of each solution was adjusted to $\mu = 0.12$ *M* with NaCl. The ion association constants K_{IP} were calculated using the reiterative graphical method of Newton and Arcand[21a] as elaborated by Davies.[21b] Constant K_{IP} values were obtained after about five reiterative graphical plots.

Results and Discussion

The equilibrium proportions of the three geometric isomers of $[Co(dien)_2]^{3+}$ under various conditions (given in Table I) were obtained by analyzing the solutions resulting from aerial oxidation of mixtures of cobalt(II) and dien in the presence of charcoal catalyst.

An alternative approach to obtaining this information, equilibration of each separate isomer to the mixture in the presence of charcoal, was also investigated.[22] It was found that equilibration of any one isomer at 18° required several months, so that it might be argued that the aerial oxidation preparations at that temperature should have been performed over a time scale similar to that of the equilibration experiments. However the isomer proportions obtained from the aerial oxidation procedures after 36 hr were identical with

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[22] G. H. Searle and F. R. Keene, unpublished results.

the equilibration results within the experimental errors, so that presumably the catalysis induced by charcoal is enhanced by the presence of the cobalt(II) in the aerial oxidation preparations.[20] At 80° the aerial oxidation preparations here reported and the charcoal-catalyzed equilibrations also gave identical values of the isomer proportions. It is also relevant to the present work that each isomer undergoes isomerization to this same mixture extremely slowly in the absence of charcoal (equilibration requires *ca.* 2 weeks at 80°).[22]

The crude $[Co(dien)_2]Cl_3$ complex (as an isomeric mixture) has been isolated in 94% yield from aerial oxidation preparations with charcoal,[9] so that it is assumed in the present isomer proportion studies that the complex was formed in solution in at least this amount. The maximum yield of cobalt(III) species anticipated would probably be ~96%, because ~4% reduction to cobalt(II) is known to occur from the analogous hexaamine system $[Co(en)_3]^{3+}$ in the presence of charcoal.[20] This isolation of the complex in high yield indicates that any errors in the determined isomer proportions arising from adsorption of the complex on the charcoal should be insignificant.

All these results, together with the observation that all charcoal-catalyzed preparations (aqueous solutions) of $[Co(dien)_2]^{3+}$ (both oxidative and substitutive) gave products of similar isomeric distribution,[8-10] provide substantial evidence that charcoal markedly catalyzes the attainment of a true thermodynamic equilibrium distribution of isomers in the $[Co(dien)_2]^{3+}$ preparations. It is generally accepted that charcoal catalyzes equilibration between cobalt(III) complexes and isomers in aqueous solution, although this function of charcoal in nonaqueous solvents has not been confirmed. For all runs by the aerial oxidation method the concentrations were adjusted to ensure that no product separated out, so that all the results correspond to equilibria in solution.

The isomer proportions were not affected by variation of cobalt concentration over the 20-fold range $[Co] = 0.4$–0.02 *M* (Table I).

Preference for the Meridional Configuration. The *mer* ligand arrangement has been indicated for the isolated mono(diethylenetriamine) complexes $[Co(dien)Cl_3]$,[23-26] $[Co(dien)(NO_2)_3]$,[23-27] $[Co(dien)(NO_2)_2Cl]$,[23] and $[Co(dien)(NO_2)_2(NH_3)]^+$,[23] and only in certain circumstances have facial mono(diethylenetriamine) complexes of cobalt(III) been observed. In the mixed bis(tridentate) systems $[Co(dien)(IDA)]^+$ [28] and $[Co(dien)(S\text{-Asp})]^+$ [29] the predominance of the facial geometric forms was attributed to the strong preference by these amino acid ligands for the less strained facial coordination. Of the mono(diethylenetriamine)cobalt(III) complexes involving three monodentate ligands however, only in $[Co(dien)(H_2O)_3]^{3+}$ and $[Co(dien)(H_2O)_2Cl]^{2+}$ have facial arrangements been reported[26,30] although these two complexes have not been isolated as solids. It is possible that the aquo ligands might enhance the stability of facial dien coordination through intramolecular hydrogen bonding or through intermolecular hydrogen bonding involving bridging solvent water molecules.[31] It is noted however that $[Cr(dien)Cl_3]$ and $[Rh(dien)Cl_3]$ have each been isolated in facial and meridional forms.[32]

Thus, there appears to be a preference for meridional coordination by dien in the above cobalt(III) complexes, although the effect of the acido substituents is not really known. This accords however with the *mer*-$[Co(dien)_2]^{3+}$ isomer being favored over the two facial forms, at least under conditions where intermolecular interactions appear to be insignificant. Under the usual preparative conditions at 18° the proportions obtained were *s-fac*:*u-fac*:*mer* = 7:28:65 for aqueous solutions (with Cl^- or Br^- as anion) and 7:14:79 for aprotic solvents (with ClO_4^- counterion). These figures will be used as references with which the other data will be compared.

The *u-fac* isomer should be favored over the *s-fac* on statistical grounds; after one dien ligand has coordinated *facially* to the metal ion, the second ligand can subsequently attach in three possible ways, leading to the distribution *s-fac*:*u-fac* = 1:2. (The *u-fac* isomer can exist as enantiomers; the s-cis cannot.[9]) This statistical ratio is reflected in the observed proportions quoted above and particularly with the aprotic solvents.

Effect of Solvation. From preparations carried out in various solvents (water, alcohols, and dipolar aprotic solvents) it was evident that the equilibrium isomer proportions were significantly dependent on the solvent. In water, ion association with chloride or perchlorate anions seems to be unimportant (Table I), and with dimethyl sulfoxide and dimethylacetamide as solvents ion association would be expected to be minimal under the perchlorate anion conditions studied.[33] The observed differences in the proportions with these two solvent types should therfore be due predominantly to solvation effects.

These differences are not large however (*s-fac*:*u-fac*:*mer* = 7:28:65 in water, 7:14:79 in aprotic solvents), and this may reflect that none of the isomers is greatly polar, so that *specific* cation–solvent interactions would not be large. The increased stability of the *mer* form in the aprotic solvents implies that this isomer is more polar than the *u-fac* (both have molecular symmetry C_2).

The proportions in methanol (18:29:53) show the *mer* isomer to be relatively less stable here. There is a correlation between the *mer* proportions observed in aprotic solvents, water, and methanol (79, 65, and 53% respectively) and the solvating powers of these solvents for cations in the order DMA, DMSO > water > methanol,[34] although the possibility of specific interactions of the complex cations with acetate ion in these methanol runs cannot be dismissed.

Effect of Perchlorate, Nitrate, Bromide, and Chloride Anions. In aqueous solution runs at 18° with the above anions or acetate present in stoichiometric quantities, the equilibrium isomer composition was independent of the anion. This accords with the relatively small variations in association constants for outer-sphere complexes between a given cobalt(III)–hexaamine type cation and the above an-

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ions, although the tabulated data are limited.[35] The addition of a large excess of any of these anions (excepting acetate) did not change the isomer proportions of $[Co(dien)_2]^{3+}$, and pmr[16] and CD[12,36] evidence indicates that excesses of these anions do not greatly change the conformer compositions in systems such as $[Co(en)_3]^{3+}$. It seems therefore that these anions do not associate greatly with these complex ions in water, or at least they show no preferred orientations.

In dimethylacetamide the ion association with chloride should be larger than in water,[33,37] and the isomer proportions in $[Co(dien)_2]^{3+}$ were considerably altered on addition of excess chloride in this solvent. In particular the *s-fac* isomer was stabilized at the expense of the *mer* (Table I).

Effect of pH. The proportion of *s-fac*-$[Co(dien)_2]^{3+}$ was raised slightly (to 12%) with excess acetate ion. In all aqueous preparations involving the other singly charged anions, the solutions had pH ~4, but the pH of the acetate solution was ~8. That this was an effect of pH rather than of acetate ion specifically was checked by basifying a chloride preparation with added sodium hydroxide when a similar change in isomer proportions was observed (Table I). Basic conditions also obtained for the preparations involving phosphate and selenite, but the greater effects in these instances were due primarily to specific ion associations which swamped any pH effect.

Specific Ion Associations with Phosphate, Selenite, and Sulfate. The greatest effects on the equilibrium isomer proportions were shown on the addition of the oxy anions SO_4^{2-}, SeO_3^{2-}, PO_4^{3-}, or HPO_4^{2-} (but not $H_2PO_4^-$), with the effect of sulfate being less than that for the other species (aqueous solutions, Table I). Under these conditions the proportion of the *s-fac* isomer increased at the expense of the *mer*, with the *u-fac* proportion remaining nearly constant. As the PO_4^{3-} concentration was increased, the proportions of isomers changed continuously from *s-fac*:*mer* = 7:65 in the "reference case" to 59:12. These observations imply that there are specific interactions between the three $[Co(dien)_2]^{3+}$ isomers and phosphate anion and that the magnitudes of the interactions are in the order *s-fac* > *u-fac* > *mer.*

Of many anions tested, phosphate and selenite (and to a lesser extent sulfate) had particularly marked effects on pmr[15-17] and CD[12,36] spectra of $[M(en)_3]^{3+}$ ions. The spectral changes observed have been interpreted as the consequence of alterations of relative conformer populations,[3,12,15-17] although ion pairs formed should also contribute direct electronic effects to the CD.[12] Although larger association effects would be expected for these more highly charged oxy anions than for singly charged anions in any case, the results have indicated that specific interactions occur such that the tris-lel[1] conformer becomes more favored relative to the other three conformers. The tris-lel conformer of $[M(en)_3]^{3+}$ has two sets of three N-H bonds aligned nearly parallel to the molecular C_3 axis, a situation which does not obtain for any of the other conformers having ob[1] rings. Mason and Norman[12] suggested that these tetrahedral oxy anions could approach the tris-lel cation along the C_3 axis and associate by hydrogen bonding to the nearly parallel N-H bonds. The structure of the proposed specifically oriented ion pair $[Co(en)_3]^{3+}$, PO_4^{3-} is shown in Figure 2.[38,39] If the predominant conformation in solution was *not* originally tris-lel but was lel$_2$ob as indicated by recent pmr studies,[15,17] then the addition of these oxy anions would stabilize the tris-lel form and decrease the proportion of lel$_2$ob. The -CH_2- resonances of the pmr spectrum should therefore be modified,[16] and the CD spectrum should change significantly.[12] The recent X-ray crystal structure analyses of $[Co(en)_3]_2(HPO_4)_3 \cdot 9H_2O$[40] and $[Co(en)_3]PO_4$[41] have shown the three chelate ring conformations to be lel and the phosphate ion to be positioned approximately on the C_3 axis of each molecule as proposed by Mason.

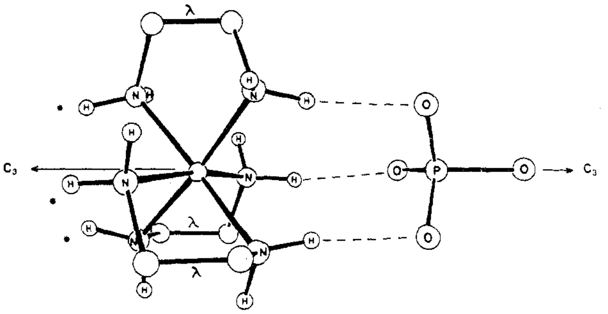

Figure 2. The structure of the ion pair between Δ-$[Co(en)_3]^{3+}$ (λλλ, tris-lel) and PO_4^{3-}, drawn using crystallographic data from G. L. Blackmer, G. H. Lin, J. L. Sudmeier, and R. M. Wing, unpublished work, private communication.

Such hydrogen-bonding capacity should depend on the basicity of the anion. Thus the reduced effect of sulfate, compared to the other oxy anions mentioned, on both $[Co(dien)_2]^{3+}$ and $[M(en)_3]^{3+}$ systems may be correlated with its being the poorest hydrogen-bond acceptor since it is the weakest base.

For the isomers of $[Co(dien)_2]^{3+}$, some association with oxy anions has been indicated previously. The CD of the *u-fac* isomer changes on addition of selenite, indicating some conformational change due to specific ion association.[42] Similarly, sulfate ion changes the CD of the *mer* form,[10] and phosphate decreases the racemization rate of this isomer.[43]

Dreiding molecular models show that the *s-fac*-$[Co(dien)_2]^{3+}$ ion has two sets of three N-H bonds (two from primary amine groups, one from secondary) appropriately disposed at opposite ends of the molecule (Figure 3) to allow hydrogen bonding in a manner analogous to that proposed above for $[M(en)_3]^{3+}$. The models indicate that while there may be some conformational flexibility within the *s-fac* arrangement, such conformational changes would not affect these N-H dispositions significantly. Figure 3[38] shows the particular conformer λδ-δλ[39] (point symmetry C_{2h}) which is that found in the crystal form[44] and which might be expected to be present in reasonable proportion in solution. Stabilization of this isomer could thus occur by ion-pair formation, with oxy anions specifically oriented through hydrogen bonding in the manner indicated in the figure.

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(35) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 37.

(36) H. L. Smith and B. E. Douglas, *J. Amer. Chem. Soc.*, 86, 3885 (1964); *Inorg. Chem.*, 5, 784 (1966).

(37) W. A. Millen and D. W. Watts, *J. Amer. Chem. Soc.*, 89, 6858 (1967).

(38) The perspective structure representations in the figures were obtained using computer drawings of crystallographic structure data. Open circles are carbon or cobalt atoms. C-H bonds are omitted for clarity. In each diagram an alternative set of N-H bonds for association with PO_4^{3-} ion is denoted with asterisks.

(39) Λ and Δ refer to absolute chelate configurations about a metal atom, and λ and δ refer to chelate ring conformations, as defined in *Inorg. Chem.*, 9, 1 (1970).

(40) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, 10, 1486 (1971).

(41) G. L. Blackmer, G. H. Lin, J. L. Sudmeier, and R. M. Wing, unpublished work.

(42) F. R. Keene, G. H. Searle, and S. F. Mason, *Chem. Commun.*, 839 (1970).

(43) G. H. Searle and F. R. Keene, *Inorg. Chem.*, 11, 1006 (1972).

(44) M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 28, 470 (1972).

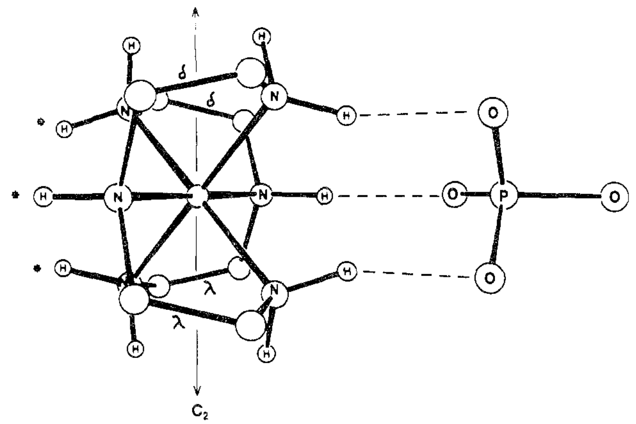


Figure 3. The proposed structure of the ion pair between *s-fac*-[Co(dien)$_2$]$^{3+}$ (λδ-δλ) and PO$_4^{3-}$. The cation structure was drawn using crystallographic data from M. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 470 (1972).

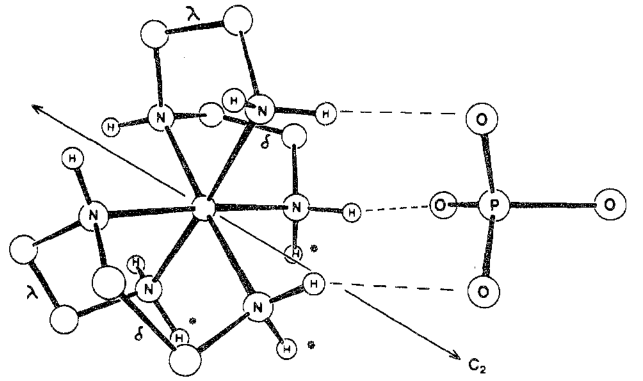


Figure 4. The proposed structure of the ion pair between *u-fac*-[Co(dien)$_2$]$^{3+}$ (Δ(δλ-δλ)) and PO$_4^{3-}$. The cation structure was drawn using crystallographic data from M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **29**, 739 (1973).

The *u-fac* isomer also has two such sets of three N-H bonds (all from NH$_2$ groups), these sets being related by the molecular C_2 axis. In this isomer however, these two potential sites for hydrogen bonding to PO$_4^{3-}$ ion are in close proximity (they are effectively on two adjacent faces of the N$_6$ octahedron). Association with one PO$_4^{3-}$ might therefore be expected to be intrinsically less favorable than for the *s-fac* isomer. In the latter isomer the two potential hydrogen-bonding sites are widely separated, so that we consider that there is a greater chance of a PO$_4^{3-}$ ion locating one of these suitable sites. The Dreiding models suggest that for the *u-fac* isomer the orientations of the N-H bonds are more dependent on the particular chelate ring conformations than in the case of *s-fac*. Figure 4[38] shows the Δ-*u-fac*[39] isomer in the δλ-δλ[39] conformation (symmetry C_2) which we consider is favorable for hydrogen bonding, and this is one of the conformational forms present in the solid state.[45]

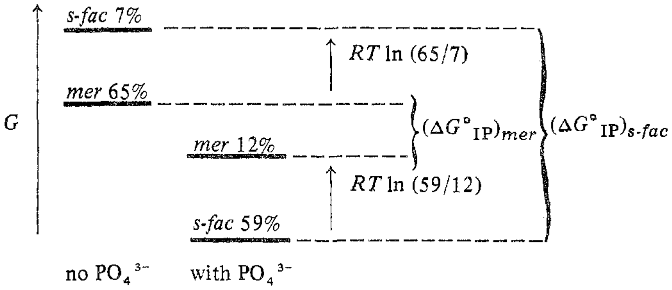
The *mer* form of the complex appears to have no such triple parallel N-H dispositions to favor strong specific association with tetrahedral oxy anions.

In [M(en)$_3$]$^{3+}$ systems, the effects of such associations are observed only as conformational changes. The [Co(dien)$_2$]$^{3+}$ system probably involves some conformational ordering also so that the particular N-H bonds in each isomer attain the most appropriate orientations for the maximum associative effects, but this is of minor importance compared with the preferential stabilization of geometric forms in the context of the present experiments. Such conformational changes probably account for the changes in CD of the *u-fac* and *mer* forms with added anions.[10,42]

We propose that these specific associations between oxy anions and the [Co(dien)$_2$]$^{3+}$ cations by hydrogen bonding through suitably disposed sets of N-H bonds can satisfactorily account for the present experimental proportions results. The study of models indicates that the existence of such N-H bond sets should lead to stabilizations of the isomers in the order *s-fac* > *u-fac* > *mer*, which is that deduced from the experimental proportions results.

If the *mer* isomer is stabilized on interaction with phosphate, to an extent designated $(\Delta G^\circ_{\mathrm{IP}})_{mer}$, then it is clear that each of the facial isomers is stabilized even more on association as their proportions increase relative to the *mer* form. This additional stabilization of the facial isomers can be evaluated from the isomer distributions already quoted (see Scheme I). $(\Delta G^\circ_{\mathrm{IP}})_{s\text{-}fac} - (\Delta G^\circ_{\mathrm{IP}})_{mer} = -RT \ln (59/12) - RT \ln (65/7) = -2.3$ kcal mol^{-1}. Similarly, $(\Delta G^\circ_{\mathrm{IP}})_{u\text{-}fac} - (\Delta G^\circ_{\mathrm{IP}})_{mer} = -1.0$ kcal mol^{-1}. The values of $\Delta G^\circ_{\mathrm{IP}}$ for the individual isomers cannot be evaluated from these data.

Scheme I



The ion association constants K_{IP} between the three isomeric cations and phosphate in aqueous solution were obtained spectrophotometrically ($\mu = 0.12\ M$ with NaCl, temperature 25.0°, pH 11.5). The values of K_{IP} thus determined for 1:1 [Co(dien)$_2$]$^{3+}$, PO$_4^{3-}$ ion pairs of the geometric isomers are 5460 (*s-fac*), 850 (*u-fac*), and 84 (*mer*). These values indicate the same order of stabilizations of the three isomers with phosphate as that deduced above from the proportions results. From these K_{IP} results the $\Delta G^\circ_{\mathrm{IP}}$ values for the isomers are calculated as −5.1 kcal mol^{-1} for *s-fac*, −4.0 kcal mol^{-1} for *u-fac*, and −2.6 kcal mol^{-1} for *mer*. The differences between these values agree well with the corresponding differences calculated above from the proportions data, particularly considering the variations in ionic strength and pH involved in the comparison.

In dimethylacetamide, similar stabilization of *s-fac* at the expense of *mer* was observed with added chloride (Table I), suggesting ion association between chloride and suitable N-H bonds of the complex isomers. The effects of oxy anions on isomer proportions could not be reliably studied in the aprotic solvents due to the reduced solubilities of the oxy anion salts of [Co(dien)$_2$]$^{3+}$ in these media. Despite some precipitation of products, solution analyses did suggest that the *s-fac* isomer was again considerably enhanced in these solvents. (These results are not given in Table I.)

Effect of Temperature. The less stable facial isomers became more favored when the aeration preparations were carried out at 80°, compared with preparations at 18° but with conditions otherwise similar (Table I). However, as little is known concerning the relative contributions of enthalpy

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[45] Y. Saito, *Proc. Int. Conf. Coord. Chem.*, 14, 91 (1972); M. Konno, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, 29, 739 (1973).

Table II. Enthalpy and Entropy Contributions to Observed Isomer Equilibria in Aerial Oxidation Preparations of $[Co(dien)_2]^{3+}$

Anion	Temp, °C	K	$\Delta G°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$-T\Delta S$, kcal mol^{-1}	$\Delta S°$, eu
			Isomer Pair *mer-u-fac*			
Cl^-	18	2.32	−0.49 ± 0.03	−2.3 ± 0.5	1.8 ± 0.4	−6 ± 1
Cl^-	80	1.15	−0.10 ± 0.03		2.2 ± 0.5	
SO_4^{2-}	18	1.41	−0.20 ± 0.03	−2.0 ± 0.5	1.8 ± 0.4	−6 ± 1
SO_4^{2-}	80	0.77	+0.18 ± 0.04		2.2 ± 0.5	
			Isomer Pair *mer-s-fac*			
Cl^-	18	9.29	−1.3 ± 0.1	−2.7 ± 1.2	1.6 ± 1.0	−5 ± 3
Cl^-	80	3.92	−1.0 ± 0.1		1.9 ± 1.2	
SO_4^{2-}	18	2.67	−0.57 ± 0.05	−1.8 ± 0.6	1.2 ± 0.5	−4 ± 2
SO_4^{2-}	80	1.55	−0.31 ± 0.05		1.5 ± 0.6	
			Isomer Pair *u-fac-s-fac*			
Cl^-	18	4.00	−0.8 ± 0.1	−0.5 ± 1.1	−0.3 ± 1.0	+1 ± 3
Cl^-	80	3.42	−0.9 ± 0.1		−0.3 ± 1.2	
SO_4^{2-}	18	1.89	−0.34 ± 0.05	+0.3 ± 0.5	−0.7 ± 0.5	+2 ± 2
SO_4^{2-}	80	2.00	−0.49 ± 0.05		−0.8 ± 0.6	

and entropy to conformational and isomeric stability, the effect of temperature could not be predicted.

The isomer ratios determined for the system $[Co(dien)_2]^{3+}$ at these two temperatures allow the separation of the free energy differences between the isomers into the enthalpy and entropy contributions. The only experimental errors involved in these determinations were in the temperature interval (±2°) and in the isomer proportion percentages which were in general reproducible to ±1. While this error in the proportions might appear reasonably satisfactory, it results in appreciable uncertainty in the derived energy values, and the maximum errors are quoted with the calculated energies in Table II. The temperature uncertainty leads to relatively small errors only. Although the present results do not therefore allow the most accurate analysis, the possibilities and limitations of this experimental approach will be apparent.

The effects of temperature variations were studied in aqueous solutions with the three different counterions chloride, acetate, and sulfate. The equilibria between the isomers in the presence of chloride and acetate were essentially the same as shown by the observed proportions (Table I), so that the thermodynamic data are given only for chloride and sulfate in Table II. The results indicate large negative entropy differences (~ -6 eu) for the equilibria *s-fac* ⇌ *mer* and *u-fac* ⇌ *mer*, but the entropy contribution to *s-fac* ⇌ *u-fac* is small. This is consistent with the *mer* form being the most ordered, which may be rationalized by the less conformational freedom than is possible in the two facial isomers of the complex. The pmr spectra[9] have also been interpreted on the basis of rapid conformational inversion in the facial forms, whereas such inversion would be restricted for the *mer* isomer under the acidic (pH 4) conditions obtaining in both the pmr spectra and the present work.

For the equilibrium in the presence of sulfate, where association occurs, the energy values suggest that the differences in proportions (compared to the chloride and acetate conditions where association is less important) may be due mainly to the enthalpy contributions. However because of the limited accuracy possible in the energy analysis this conclusion must at present be viewed with some caution. The greater associative effects shown by the anions selenite and phosphate could not be examined at 80° since the basic solutions containing these ions induced decomposition of the cobalt complex at this temperature.

Minimized calculations of the intramolecular enthalpies of the isomers of $[Co(dien)_2]^{3+}$ have predicted that on this basis the three geometric isomers should be of comparable stabilities.[19] The strain energies thus calculated are 9.6, 9.6 and 9.7 kcal mol^{-1} for the *s-fac, u-fac,* and *mer* isomers, respectively, but it is uncertain whether these minimization values relate to the same energy zero.[18,19]

While the differences ($\Delta H°$) between isomer pairs from these calculations are in qualitative agreement with the experimental isomer distribution ($\Delta G°$),[19] this correlation may be fortuitous as the present thermodynamics results show that both the entropy and enthalpy contribute significantly, but in opposition, to $\Delta G°$ for the *u-fac* ⇌ *mer* and *s-fac* ⇌ *mer* equilibria (Table II). The comparisons of the calculated intramolecular $\Delta H°$ values between isomer pairs with the present experimental (intramolecular and intermolecular) $\Delta H°$ values reveal some disparities outside the limits of our experimental errors. These disparities are probably a result of the comparisons of the calculated free ion and equilibrium measurements on the ion in its solution environment.

For these various reasons, present minimization calculations would not seem to be greatly reliable for predicting the relative stabilities of geometric isomers under practical solution conditions. Work is continuing on the calculative method and on the minimization assessment of interionic factors.[46]

Modified Preparation of the *s-fac* Isomer. The present work demonstrates that ion association might sometimes be applied to advantage in obtaining less stable isomers of metal complex systems. Such effects have also been noted previously.[47] For optimum yield (59%) of the *s-fac*-$[Co(dien)_2]^{3+}$ isomer the aerial oxidation preparation[9] with charcoal may be carried out in aqueous 0.1 *M* sodium phosphate at room temperature, the product solution being absorbed on a large column of SP-Sephadex C-25 and eluted with 0.3 *M* sodium tartrate solution. The first eluted *s-fac* band can then be reabsorbed on a short column of a weak-acid cation exchanger (Bio-Rex 70, analytical grade, 50-100 mesh, in the sodium form), washed with water, and eluted with 0.1

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(46) M. Dwyer and M. R. Snow, work in progress.

(47) E. W. Gillow and G. M. Harris, *Inorg. Chem.*, 7, 394 (1968).

M hydrobromic acid. The eluate on evaporation yields crystals of *s-fac-*$[Co(dien)_2]Br_3$.

Acknowledgments. We are grateful for the use of facilities at the Research School of Chemistry, Australian National University, Canberra, to complete some of the experimental work (F. R. K.). We thank Dr. D. W. Watts (University of Western Australia) for valuable discussions and for advice on the ion association constants measurements and Dr. G. Gainsford (Australian National University) for assistance in preparing the figures. dien was kindly provided by Union Carbide (Australia) Ltd.

Registry No. *s-fac-*$[Co(dien)_2]^{3+}$, 38318-04-6; *u-fac-*$[Co(dien)_2]^{3+}$, 38318-05-7; *mer-*$[Co(dien)_2]^{3+}$, 38318-06-8; ClO_4^-, 14797-73-0; NO_3^-, 14797-55-8; CH_3COO^-, 71-50-1; Br^-, 24959-67-9; Cl^-, 16887-00-6; SO_4^{2-}, 14808-79-8; SeO_3^{2-}, 14124-67-5; HPO_4^{2-}, 14066-19-4; PO_4^{3-}, 14265-44-2.

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Polarographic Study of Metal Complexes. XII.[1] Pentacyanocobaltate(III) Complexes

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The pentacyanocobaltate(III) complexes of the $[Co(CN)_5X]$ type are reduced in one or two steps to the $[Co^I(CN)_5]^{4-}$ ion leaving the sixth ligand, X^{m-}, at the dropping mercury electrode (dme), where the ligand X denotes the ion I^-, Br^-, Cl^-, SCN^-, NO_2^-, N_3^-, $S_2O_3^{2-}$, or SO_3^{2-}. The evidence from which we drew this conclusion was provided with the anodic wave responsible for the ligand X liberated from the Co(I) complex. The $[Co^I(CN)_5H]^{3-}$ formula has been widely accepted as a final reduction product. In this work, however, the stoichiometric relation between $[Co^I(CN)_5]^{4-}$ and H^+ ion was determined to be always 2:1, suggesting a dimeric configuration of the pentacyanocobaltate(I) ion in neutral and acidic solutions. The $[Co^I(CN)_5\text{-}H\text{-}Co^I(CN)_5]^{7-}$ ion is neither reducible nor oxidizable electrochemically at the dme. Two conclusions were drawn about the anodic oxidation of $[Co^I(CN)_5]^{4-}$. One of them is that the electron transfer from 3d orbitals of cobalt to mercury atoms can proceed only through the $[(CN)_5Co^I\text{-}Hg]$ intermediate. The other is that the peculiar feature of $[Co^I(CN)_5]^{4-}$ of extracting a proton from water molecules can be attributed solely to the trans influence of the fifth cyanide.

Introduction

The question of the composition and structure of the pentacyanocobaltate(I) ion formed by the reduction of pentacyanocobaltate(II) and -cobaltate(III) complexes still remains in a controversial state in spite of a number of works done on this subject.[2] Moreover, there are conflicting views about the oxidation state of the pentacyanocobaltates formed from $[Co^{II}(CN)_5]^{3-}$ and hydrogen gas, by the disproportionation of $[Co^{II}(CN)_5]^{3-}$ in aqueous solution or by the chemical reduction of $[Co^{II}(CN)_5]^{3-}$ with $NaBH_4$, Na-Hg amalgam, etc.[3-5] The $[Co^I(CN)_5H]^{3-}$ formula has been widely accepted as a final reduction product since Griffith and Wilkinson[6] proposed it on the basis of the proton nmr spectrum. In addition, it has already been established that the reaction between $[Co^I(CN)_5]^{4-}$ and H^+ ion can proceed in water.

The cathodic reduction of pentacyanocobaltate(III) complexes has briefly been reported previously.[7,8] Hence, the present paper chiefly deals with the composition and structure of the pentacyanocobaltate(I) ion formed by the cathodic reduction at the dropping mercury electrode (dme).

Experimental Section

The preparation of pentacyanocobaltate(III) complexes was carried out according to the scheme of reactions

$$\textit{trans-}[Co(CN)(SO_3)(NH_3)_4]\cdot 2H_2O \rightarrow$$

$$\textit{trans-}[Co(CN)(OH_2)(NH_3)_4]Cl_2{}^{9} \xrightarrow[\text{or KX}]{\text{NaX}}$$

$$\textit{trans-}[Co(CN)X(NH_3)_4]^{q+} \xrightarrow{4KCN} K_n[Co(CN)_5X]$$

where the ligand X represents the ion I^-, N_3^-, NO_2^-, $S_2O_3^{2-}$, or SCN^-. The novel intermediate complexes of the trans-$[Co(CN)X(NH_3)_4]$ type[10] were prepared by treating the monocyanoaquotetraamminecobalt(III) chloride[9] with sodium or potassium salt of the ligand in excess at 80–95° for 1 hr. The absorption spectra in visible and uv regions of the $[Co(CN)X(NH_3)_4]$ complexes showed that the first spin-allowed d-d band shifts toward the direction of a shorter wavelength in the following order of the ligand X: N_3^-, CO_3^{2-}, $NH_2C_2H_5$, py, NH_2CH_3, NCS^-, NH_3, NO^-, SO_3^{2-}, CN^-, PPh_3.

The order of this spectrochemical series suggests the complexes to have a trans configuration rather than a cis one, since it is in agreement with that of the tetraamminecobalt(III) complexes with a trans configuration. That is, no isomerization occurs during the substitution reaction. The monocyanotetraamminecobalt(III) complexes were recrystallized from hot water containing 6% acetic acid except for the complexes with $X = S_2O_3^{2-}$ and CO_3^{2-}. The former complex is quite insoluble both in water and in organic solvents. The results of elementary analyses only for the novel intermediate complexes are available (see paragraph at end of paper regarding supplementary material).

The finally desired pentacyanocobalt(III) complexes were prepared by treating these monocyanotetraamminecobalt(III) complexes with the calculated amount of KCN at optimum temperatures. For the pentacyano complex with $X = I^-$, the reaction proceeded gently still at 0°, while that for $X = N_3^-$ or SCN^- proceeded at 50–60°. For X =

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[9] H. Siebert, *Z. Anorg. Allg. Chem.*, 327, 63 (1964).

[10] The novel monocyano complexes of this type other than these have also been prepared and identified by elementary analyses: $X = PPh_3$ (triphenylphosphine), NO^-, py (pyridine), $NH_2C_2H_5$, NH_2CH_3, or CO_3^{2-}.