

The present structural analysis provides additional evidence for our contention^{8,10,11} that the major reason for the presence of Gla rather than Glu in calcium-binding proteins is the availability in the former of additional carboxylate moieties that can permit the formation of extensive polymeric arrays of the general kinds found in all of these model complexes. The ability of a metal ion to participate in such aggregation is limited by its ability to adopt a wide variety of geometries, since in the protein the environments available to the metals would surely be irregular. The great flexibility of calcium(II), in contrast to the rigid requirement of precise octahedral geometry for magnesium(II), may allow the protein to discriminate between calcium and magnesium, since the formation of complex polymeric arrays involving magnesium is precluded by the geometric constraints of that metal ion.

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Supplementary Material Available: Tables S1 (anisotropic and isotropic thermal parameters) and S2 (hydrogen-bonding distances and angles) (2 pages); Table S3 (observed and calculated structure amplitudes) (8 pages). Ordering information is given on any current masthead page.

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Li₂F⁺ and Li₂OH⁺ in Molten Alkali-Metal Nitrate

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Introduction

Polymetal complexes of the type M_mX^{m+} (X = halide or chalcogenide) are known to play an important role in the solution chemistry of certain mixed molten salt systems and concentrated aqueous solutions.^{1–6} Ionic molten salt solvents probably enhance the stability of such polymetal species, which until 1988 were thought to be formed preferably between soft acceptor and donor ions. Iodide complexes with the d¹⁰ ions Hg²⁺ and Ag⁺ are typical examples,^{1–3} but we have recently also characterized Tl₂Br⁺ in molten alkali-metal nitrates.⁷

A further extension of the search for polymetal complexes into the d^{10s} metal ion chemistry revealed that Pb²⁺ forms Pb₂X³⁺ with halide and hydroxide ions in nitrate melts with the overall thermodynamic stability increasing in the X sequence Cl < Br < I ≈ F ≪ OH.^{4,5,8} Hence, the hard donors F⁻ and OH⁻ can give polymetal complexes of equal or even higher stability than analogous species with softer halides. On the other hand, a thorough thermodynamic and X-ray scattering investigation into the Cd(II) chemistry in nitrate-based melts with compositions that were optimized to yield polycadmium halide complexes gave

conclusive evidence for the complete absence of complex species other than CdX⁺ (X = F, Cl, Br, or I).⁹ A d¹⁰ valence electron configuration is thus neither sufficient nor necessary for polymetal complexation in the melts.

It has been argued that the effects of cation repulsion may severely reduce the tendency to form polymetal species with a high formal positive ionic charge.¹⁰ The absence of e.g. Cd₂X³⁺ species could of course be explained with such arguments. The stability of Pb₂F³⁺ and Pb₂OH³⁺ has been attributed mainly to direct Pb–Pb bonds, the formation of which must energetically compensate for the repulsion.^{6,8} Further work along these lines has recently revealed that the s²p⁶ ions Sr²⁺ and Ba²⁺ form M₂F³⁺ in nitrate melts.¹¹ The extent of direct metal–metal interaction in these complexes is indeed unknown, and no straightforward bonding scheme for polymetal complexes seems to be attainable at present. However, the very fact that the alkaline-earth metal ions do yield M₂F³⁺ species makes the corresponding “low-charge” Li⁺ systems highly interesting objects of study. A paramount matter of interest is of course to what extent direct Li–Li interactions may be of importance.

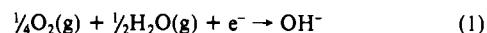
Considering the relevant solution chemistry for Li⁺ in water and other molecular solvents, it seems that only one single complex species, viz. LiOH(aq), has been observed.^{12–15} No fluoride complexes have been detected.

The aim of the present work is to clarify the possible existence of polyolithium complexes Li_mX^{m–1} in the melts by potentiometric determination of X⁻ (X = F or OH) activity changes in systems [(K,Na),Li][X,NO₃] with the total concentration relation C_{Li} > C_X.

Experimental Section

Chemicals. KNO₃ and NaNO₃ (Merck, p.A.) were dehydrated at 130 °C. KF and LiNO₃ were dried under vacuum at increasing temperatures up to 130 °C. Karl Fischer titrations showed the water content of LiNO₃ to be less than or equal to the detection limit of the method of analysis (≤1.0 × 10⁻² wt %). The chemicals were handled in a glovebox with a dry N₂(g) atmosphere. The NaOH preparation (EKA, p.A.) contained 95.7 wt % sodium hydroxide, as determined by standard acid–base titration, and water to 100.0 wt %. The O₂(g) used (Alfax, Oxygene N48; H₂O < 2 ppm, CO₂ < 0.2 ppm) was passed through Carbosorb (BDH Chemicals, 10–20 mesh) and drying agents before being equilibrated with pure water at 18.6 °C, giving the partial pressures P(H₂O) = 16 mmHg and P(O₂) ≈ 744 mmHg.

Emf Measurements. The complex formation between Li⁺ and F⁻ and between Li⁺ and OH⁻ was studied at temperatures between 240 and 290 °C. Further details about the apparatus, cell construction, and measurement procedures have been thoroughly described previously.^{4,8} The fluoride systems were studied with a LaF₃ membrane electrode,⁴ and hydroxide activities were measured with a mixed O₂/H₂O gas electrode.⁸ This [O₂ + H₂O](g),Pt(s)/OH⁻ electrode has been shown to respond reversibly to OH⁻ according to the one-electron mechanism



The total concentrations used were $1.12 \times 10^{-3} \leq C_{\text{OH}^-}/(\text{mol kg}^{-1}) \leq 1.99 \times 10^{-2}$, $2.50 \times 10^{-3} \leq C_{\text{F}^-}/(\text{mol kg}^{-1}) \leq 1.04 \times 10^{-2}$, and $8.97 \times 10^{-3} \leq C_{\text{Li}^+}/(\text{mol kg}^{-1}) \leq 1.01$. The large majority of experimental points had $C_{\text{Li}^+}/(\text{mol kg}^{-1}) \leq 0.10$.

Raman Spectroscopy. The furnace and experimental technique were analogous to those reported in earlier publications.^{8,9} Only LiNO₃–(K,Na)NO₃ and LiOH–LiNO₃–(K,Na)NO₃ melts were investigated, due to the low solubility of LiF.

Results

Potentiometric Measurements. Emf changes are observed when LiNO₃ is added to the (K,Na)(NO₃,X) melts (X = F, OH). These

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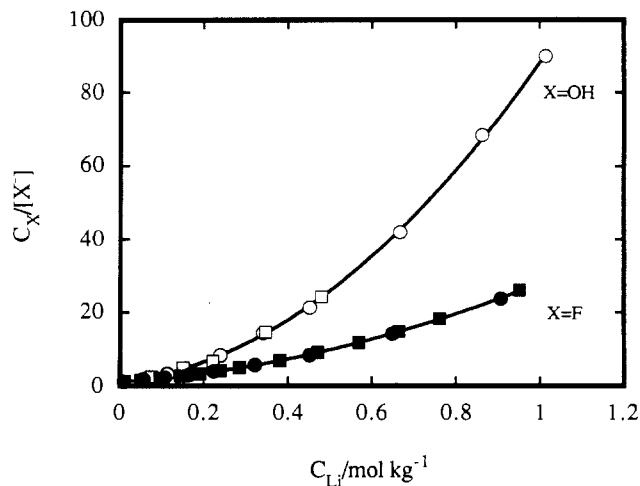


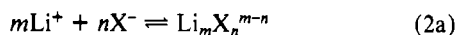
Figure 1. Experimental values of $C_X/[X^-]$ vs C_{Li} at different total concentrations of central anion X^- (F^- or OH^-): $C_F = 10.4 \times 10^{-3} \text{ mol kg}^{-1}$ (\bullet), $C_F = 2.5 \times 10^{-3} \text{ mol kg}^{-1}$ (\blacksquare), $C_{OH} = 19.9 \times 10^{-3} \text{ mol kg}^{-1}$ (\circ), and $C_{OH} = 1.1 \times 10^{-3} \text{ mol kg}^{-1}$ (\square).

Table I. Overall Stability Constants for LiX and Li_2X^+ ($X = F$ or OH) in Equimolar $(K,Na)NO_3(l)$ between 240 and 290 °C^a

$t/^\circ\text{C}$	X	$\beta_{11}/(\text{mol}^{-1} \text{ kg})$	$\beta_{21}/(\text{mol}^{-2} \text{ kg}^2)$	no. ^b
240	F	11.1 ± 0.2	23.3 ± 0.6	30
260	F	9.9 ± 0.3	17.6 ± 1.0	28
280	F	9.6 ± 0.4	16.3 ± 0.9	22
	OH	15 ± 4	69 ± 13	20
290	F	8.4 ± 0.1	13.5 ± 0.3	14

^aThe error limits define a 95% confidence interval. ^bNumber of degrees of freedom.

changes are assumed to be caused by a change in fluoride/hydroxide activity due to complex formation reactions like



with the overall stability constant

$$\beta_{mn} = \frac{[Li_mX_n^{m-n}]}{[Li^+]^m[X^-]^n} \quad (2b)$$

The emf data and total concentrations contain the information for evaluation of speciation and relevant stability constants from the sum

$$C_X = \sum_{m,n} n[Li_mX_n^{m-n}] = \sum_{m,n} n\beta_{mn}[Li^+]^m[X^-]^n \quad (3)$$

The proper complexation model was obtained graphically. It appeared that all emf data could be excellently described by

$$C_X/[X^-] = \sum_{m=0}^2 \beta_{m1}[Li^+]^m \quad (4)$$

i.e. both LiX and Li_2X^+ exist under the conditions of the study and no polyfluoride or polyhydroxide species can be detected. This is obvious from the data in Figure 1, which shows that $C_X/[X^-]$ is independent of C_X (and hence $[X^-]$) within the concentration ranges studied. A least-squares program, EMFALL, was used to evaluate the β_{m1} values.

The results of the least-squares refinements are shown in Table I. The large experimental errors for the hydroxide system unjustifies a more extensive study at different temperatures, aimed at the calculation of standard enthalpies and entropies for the complexation reactions.

The fractions α_{m1} of the total concentrations of fluoride or hydroxide in Li_mX^{m-1} defined as

$$\alpha_{m1} = \frac{[Li_mX^{m-1}]}{C_X} \quad (5)$$

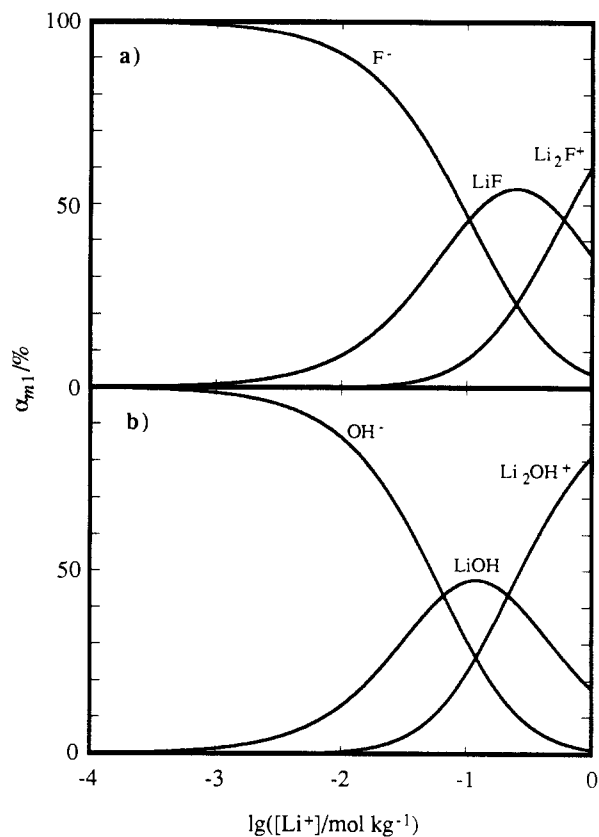


Figure 2. Fraction α_{m1} of X^- in different Li_mX^{m-1} complexes in molten equimolar $(K,Na)NO_3$ at 280 °C: (a) $X^- = F^-$ and (b) $X^- = OH^-$.

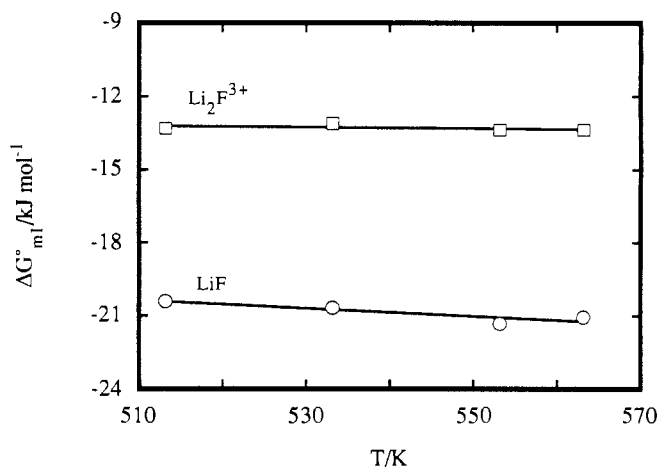


Figure 3. ΔG_{m1}^0 vs T for the stepwise formation of Li_mF^{m-1} in molten equimolar $(K,Na)NO_3$ in the temperature range 240–290 °C. The standard state is unity mole fraction.

Table II. Standard Enthalpy and Entropy Changes for the Stepwise Formation of Li_mF^{m-1} in Molten Equimolar $(K,Na)NO_3$ between 240 and 290 °C

reaction	$\Delta H_{m1}^0/\text{kJ mol}^{-1}$	$\Delta S_{m1}^0/(\text{J K}^{-1} \text{ mol}^{-1})^a$
$Li^+ + F^- \rightarrow LiF$	-13 ± 2	15 ± 3
$Li^+ + LiF \rightarrow Li_2F^+$	-13 ± 1	0 ± 2

^aThe standard state refers to unity mole fraction. The errors are ± 1 mean deviation.

are shown in Figure 2. The stepwise complexation proceeds in a similar manner in both systems, with LiX amounting to roughly 50% of X at most and Li_2X^+ being the dominating complex for $[Li^+] > 0.5 \text{ mol kg}^{-1}$.

From the temperature dependence of $\Delta G_{11}^0 = -RT \ln \beta_{11}$ and $\Delta G_{21}^0 = -RT \ln (\beta_{21}/\beta_{11})$, the standard enthalpy and entropy

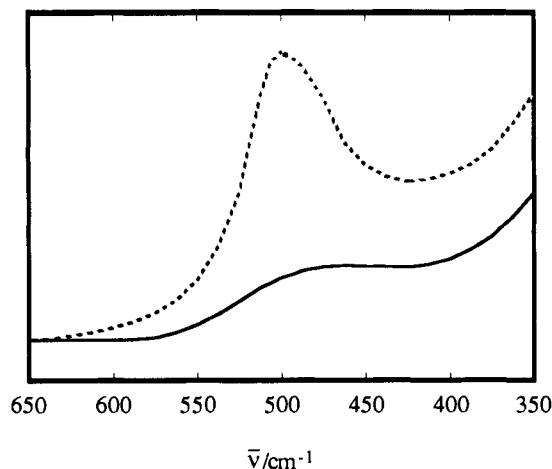
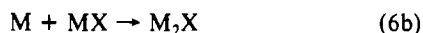


Figure 4. Raman spectral features around 500 cm^{-1} of 2 mol kg^{-1} LiNO_3 in $(\text{K,Na})\text{NO}_3(\text{l})$ at 280 $^\circ\text{C}$, before (dashed line) and after (solid line) addition of 0.6 mol kg^{-1} NaOH .

changes of the stepwise formation of LiF and Li_2F^+ , according to the schematically written reactions (6), can be determined. The



$\Delta G^\circ_{m1}(T)$ data are well described by a linear model, as seen in Figure 3. The thermodynamic parameters, obtained from linear regression, are displayed in Table II.

Raman Spectroscopy. The degeneration of nitrate D_{3h} symmetry to C_{2v} or C_s upon the introduction of LiNO_3 to a $(\text{K,Na})\text{NO}_3$ melt is similar to what has previously been observed for the corresponding $\text{Pb}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ and $\text{Cd}(\text{NO}_3)_2$ - $(\text{K,Na})\text{NO}_3$ melts, apart from the additional strong 495- cm^{-1} peak, which is assigned to $\text{Li}^+-\text{NO}_3^-$ vibrations (see Figure 4).^{6,9}

The addition of hydroxide to the melts containing lithium showed only indirect evidence of complex formation. The internal nitrate bands were restored toward those of pure $(\text{K,Na})\text{NO}_3(\text{l})$. This effect was also observed for the lead(II) hydroxide system.⁸ The intensity of the 495- cm^{-1} peak was heavily reduced, as seen in Figure 4. No direct Li^+-OH^- vibration could be detected though. An O-H stretch band was observed at 3640 cm^{-1} , unshifted relative to that of the reference sample of $\text{NaOH}-(\text{K,Na})\text{NO}_3$.⁸ The intensity of the O-H stretch band indicates that all hydroxide remains undissociated upon complex formation with lithium(I), which is also in accordance with previous observations for the lead(II) hydroxide system in $(\text{K,Na})\text{NO}_3$.⁸

Discussion

Nitrate Coordination. Electron scattering experiments on $\text{LiNO}_3(\text{g})$ indicate a monodentate association mode with a Li-O distance of 1.60 \AA and a Li-O-N angle of 105 $^\circ$ with the lithium ion slightly out of the nitrate plane, giving the molecule a C_s symmetry.¹⁶ An ab initio calculation on the other hand favors the in-plane coordination of the lithium atom, symmetrically binding to two nitrate oxygens at 1.81 \AA , which gives a C_{2v} symmetry. The experimental results are claimed to be caused by the presence of LiNO_3 dimers.¹⁷ The Raman spectroscopy results on the LiNO_3 - $(\text{K,Na})\text{NO}_3$ melts suggest, in analogy with the nitrate coordination mode to silver(I), cadmium(II), thallium(I), and lead(II) ions in molten $(\text{K,Na})\text{NO}_3$, the presence of nitrate-solvated Li(I) with a two-dentate NO_3^- coordination.^{1,6,7,9} No liquid X-ray scattering study was considered, due to the low scattering power of the lithium ion.

Dilithium Complexes. A question of major concern is whether the Li_2X^+ species in molten $(\text{K,Na})\text{NO}_3$ are stabilized by a direct Li-Li interaction. The structures of Li_2F^+ and Li_2OH^+ in the

Table III. Li-X Distance and Li-X-Li Bond Angle from Theoretical Calculations on the Li_2X^+ Ion

ion	$d_{\text{Li-X}}/\text{\AA}$	Li-X-Li/deg	method	ref
Li_2F^+	1.81	156	semiempirical	33
	1.55	180	ab initio	34
	1.68	180	ab initio	35
	1.64	180	ab initio	36
Li_2OH^+	1.76	137	ab initio	37

melts are, however, not known. Theoretical calculations, cited in Table III, indicate that an isolated Li_2F^+ ion is linear, but in a nitrate melt the structural influence of surrounding nitrates can of course not be neglected. A bridging nitrate oxygen may cause a bent structure like the one observed for Pb_2F^{3+} in nitrate melts.

A few solid compounds exhibit very short Li-Li distances, the most simple ones are $\text{LiF}(\text{s})$ [2.84 \AA], $\text{Li}_2\text{O}(\text{s})$ [2.32 \AA], and $\text{LiOH}(\text{s})$ [2.51 \AA],¹⁸⁻²² with Li-Li separations even shorter than in the pure metal Li(s) [3.04 \AA].¹⁸ The structure of $\text{LiOH}(\text{s})$ is especially intriguing, since it is analogous to tetragonal $\text{PbO}(\text{s})$, which represents the fundamental pattern for almost all lead(II) oxide and hydroxide structural chemistry.⁸ The PbO structure has been interpreted in terms of direct Pb-Pb interactions,²³ and the same type of bonding conditions may be of importance also in solid LiOH . The relatively long Li-O distances that are observed in solid Li_2O have been accounted for as a result of substantial Li-Li interaction, and the same bonding conditions have been considered for related compounds like $\text{Li}_3\text{N}(\text{s})$.²⁴

Li_2 clusters are formed in liquid NH_3 , and probably also in Li-LiX melts ($\text{X} = \text{halide}$).²⁵ The existence of Li_4 clusters with a planar ring structure and a Li-Li distance of 2.7 \AA has also been claimed.^{26,27} Li_m clusters may be stabilized by suitable second-row atoms, giving Li_mA ($\text{A} = \text{C, N, O, or F}$ and $m = 1-6$).²⁸⁻³² The stabilities of these compounds are thought to originate from Li-A bonding at low m and Li-Li bonding at higher m . Several papers also report results for the corresponding cations and anions.^{30,31,33-37} Ions of this type are frequently encountered in mass spectroscopy and molecular beam experiments.

The lack of experimental structural data for the Li_2F^+ and Li_2OH^+ complexes in $(\text{K,Na})\text{NO}_3$ melts leaves a discussion of the possibility of direct Li-Li interactions to be based on thermodynamic evidence alone. The pattern of standard free energy changes for the two complexation steps (6), may be compared with that for formation of Pb_2F^{3+} in nitrate melts at the same temperature. The very short Pb-Pb distance has been taken as an indication of metal-metal interaction, which might be expected to give an enhanced stability of Pb_2F^{3+} relative to PbF^+ . The quotient K_1/K_2 of successive stepwise stability constants is, how-

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ever, remarkably high, 200, for the Pb–F system. On the other hand, K_1/K_2 for the Li–F and Li–OH systems is 6 and 3, respectively. The values for the Li systems are close to what is expected from a random cationic ligand exchange situation where only direct metal–anion interactions are operative, i.e. the case of an ideal quasi-lattice ligand exchange.³⁸ A coordination number, Z , of 4 gives $(K_1/K_2)_{\text{theor}} \approx 3$ and a specific quasi-lattice interaction energy parameter for the cation exchange in steps 6a and 6b of $-14 \pm 2 \text{ kJ mol}^{-1}$ for the Li–F and $-17 \pm 2 \text{ kJ mol}^{-1}$ for the Li–OH system. The fact that the exchange interaction energy is largely the same in both steps 6a and 6b for either system further suggests that the same solvent cation (Na^+ or K^+) is exchanged for Li^+ in every step.

The thermodynamic parameters obtained from the temperature dependence of ΔG°_{m1} in fact confirm these results. The ΔH°_{m1} values are in close agreement with the specific interaction energy parameter for the lithium fluoride system. Consequently, the ΔS°_{m1} changes obtained are also nearly identical with the ideal configurational entropy values predicted by a quasi-lattice model approach ($Z = 4$).

It was demonstrated for the Pb(II) systems, however, that the $\Delta H^\circ - \Delta S^\circ$ patterns for the single complexation steps, as estimated from the temperature dependence of the standard free energy changes, clearly show the second step (6b) to be favored by a negative ΔH° in spite of the strong cation–cation repulsion. The ΔS° does not contribute significantly to the stability of M_2X . A positive entropy contribution from the release of coordinated nitrate ions is thought to be balanced by a negative configurational entropy change, yielding a ΔS° close to zero, which—by coincidence—almost agrees with the quasi-lattice model prediction.

This interpretation of the thermodynamics of step 6b for the Pb–F system is based on our knowledge of the structure of Pb_2F^{3+} , which indicates that a direct Pb–Pb bond is formed in the second complexation step. In the Li_2X^+ ions ($\text{X} = \text{F}$ or OH), there is, in contrast, no thermodynamic evidence of any stabilizing Li–Li bond.

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Stereospecificity in the Synthesis of the Tris(*R*)-cysteinato-*N,S*- and Tris(*R*)-cysteinesulfinato-*N,S*)cobaltate(III) Ions

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Tris(bidentate ligand)metal complexes can exist in Λ and Δ catoptric forms, and if the bidentate ligand is unsymmetrical, there are *fac* and *mer* isomers to consider as well. Furthermore, if the bidentate ligand is chiral, there will exist a diastereomeric form for each hand of the ligand. The case of three (*R*)-cysteine ligands coordinated to cobalt(III) is an especially interesting one because, in addition to the above possibilities for isomerism, there are the prospects for *N,S*-, *N,O*-, or *S,O*-chelation, leading to a total of $2 \times 2 \times 3 = 12$ possible isomers, for a given absolute configuration of the cysteine ligand. Tridentate chelation is another prospect,¹

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but the question of specificity, which this note addresses, does not arise here because (*R*)-cysteine can wrap in only one way on a face of an octahedron.

The synthesis of the green tris(*R*)-cysteinato)cobaltate(III) complex $[\text{Co}((R)\text{-cysS-}N,S)_3]^{3-}$ was described long ago,² and it has been claimed that not only does the cysteine ligand bind N,S^{3-5} but also the *fac* isomer seems to be formed exclusively over the *mer* form. Similar claims have been made in a study dealing with the related complexes of cysteine methyl ester⁶ and cysteamine,⁷ work substantiated by single-crystal X-ray studies of some of their derivatives.^{8,9}

The $[\text{Co}((R)\text{-cysS})_3]^{3-}$ ion constitutes a tris-*gauche* ring system with three equatorial carboxylate substituents (rendering each ring λ), and it would be expected to favor the Δ - $\lambda\lambda\lambda$ configuration (*lel*)₃.^{10,11} Gillard and Maskill¹² have claimed that the synthesis of the tris(*R*-cysteine) complex is stereospecific and that the Δ -*RRR* form is formed exclusively over its Λ -*RRR* diastereomer. A similar claim has been made for the uncharged tris complex $[\text{Co}((R)\text{-MecysS})_3]$ of its *O*-methyl ester.⁶ In our view this question has never been settled unambiguously. Conclusions have been based upon the composition of isolated materials without regard to yield or to the prospect of a second-order¹³ asymmetric synthesis.

The specificity of the synthesis is an important question for a number of reasons. For example, the rationalization of the product distribution for oxidation at sulfur,⁶ whereupon up to three chiral sulfenate centers arise, rests with the assumption that the starting material is itself a single diastereomer. Furthermore, the peroxidized derivative $[\text{Co}((R)\text{-cysSO}_2\text{-}N,S)_3]^{3-}$ appears¹⁴ to be a useful resolving agent, and the success of resolutions using this ion could hinge critically on the diastereomeric purity.

Results and Discussion

The complex $\text{K}_3[\text{Co}((R)\text{-cysteinato-}N,S)_3] \cdot 6\text{H}_2\text{O}$ is synthesized from (*R*)-cysteine and a suitable Co(III) precursor such as $[\text{Co}(\text{NH}_3)_6]^{3+}$.^{2-5,12,14} The complex can also be synthesized from Co(III) reactants such as $\text{Na}_3[\text{Co}(\text{OCO}_2)_3]$, $\text{K}[\text{Co}(\text{edta})] \cdot 2\text{H}_2\text{O}$, or *trans*- $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$, by direct substitution using free (*R*)-cysteine.¹⁵ Schubert² originally synthesized the tris complex from Co(II) reactants and free (*R*)-cysteine by aerial oxidation in the usual way, and presumably equilibrium between the various possible isomers is achieved under these conditions.

In our hands the synthesis of the tris complex by the original route using Co(II) and free (*R*)-cysteine gave a high yield of a dark olive green complex. For the potassium salt, high-resolution ¹³C NMR spectroscopy (Figure 1; lower spectrum)¹⁶ of a D_2O

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- (16) In D_2O at 25 °C, the ¹³C chemical shifts downfield from dioxane are as follows. $\text{K}_3[\text{Co}((R)\text{-cysS})_3]$: Δ , δ 111.75 (CO_2^-), -0.02 (CH), -31.77 ($-\text{CH}_2\text{S}^-$); Λ , δ 112.47 (CO_2^-), -3.49 (CH), -31.85 ($-\text{CH}_2\text{S}^-$). $\text{K}_3[\text{Co}((R)\text{-cysSO}_2)_3]$: Δ , δ 107.15 (CO_2^-), -0.46 (CH), -13.18 ($-\text{C}-\text{H}_2\text{S}^-$); Λ , δ 108.87 (CO_2^-), 1.53 (CH), -15.05 ($-\text{CH}_2\text{S}^-$).
- (17) The complex is reported⁴ as stable only in basic solution in the presence of excess cysteine. We find the purified complex to be stable at least in the pH range 7–13 over several hours.