Contribution from the Department of Chemistry,
The University of Kansas, Lawrence, Kansas 66045

Cotton Effect–Configuration Relationships in Mixed-Ligand Complexes.
2. The Series Cr(β-diketonate)$_n$((S)-α-amino acidate)$_{3-n}$

STEPHEN S. MINOR, GISELA WITTE,[1] and GROVER W. EVERETT, Jr.*

Received February 24, 1976 AIC60145O

Mixed-ligand complexes of the type Cr(acac)$_2$(L), where acac is the anion of 2,4-pentanedione and L is the anion of (S)-alanine, (S)-valine, or (S)-phenylalanine, have been synthesized by photolysis of Cr(acac)$_3$ in the presence of amino acid and base. In each case the two diastereomers of Cr(acac)$_2$(L) can be separated by chromatography on silica gel. Absolute configurations of these diastereomers are assigned from comparison of their CD spectra with those of the resolved parent Cr(β-dik)$_3$ complexes and from comparison of their chromatographic behavior with that of the corresponding Co(acac)$_2$(L) diastereomers reported previously. Two diastereomers of Cr(S-ala)$_3$ have been isolated, and the absolute configuration of one of these is assigned from comparison of its x-ray powder pattern with those of the four diastereomers of Co(S-ala)$_3$.

Empirical relationships between signs of Cotton effects in the ligand field region and absolute configuration are well established for certain classes of cobalt (III) complexes.[2] In part 1 of this series it was shown that such relationships derived from a combination of physical methods for tris(β-diketonato)cobalt(III), tris(1,2-diamine)cobalt(III), and tris(S-α-amino acidato)cobalt(III) complexes can be extended to Co(III) complexes having mixtures of these ligands.[3]

Less effort has been expended thus far in establishing similar Cotton effect–configuration relationships for complexes of Cr(III). Absolute configurations of tris(β-diketonato)chromium(III) and tris(1,2-diamine)chromium(III) complexes may be assigned with confidence from CD spectra in the visible region.[4–7] Also, optically active forms of the mixed-ligand species Cr(β-dik)(en)$_2$ (dik = diketonate) and Cr(β-dik)$_2$(en) have been prepared, and their CD spectra have been analyzed.[8] However, the tris complexes of α-amino acids have not been fully characterized. Indeed, although four diastereomers are possible for tris((S)- or (R)-α-amino acidate)chromium(III), only one isomer has been obtained in each case for a number of α-amino acids.[9]

The present paper is concerned with the series Cr(β-dik)$_n$(S-α-AA)$_{3-n}$ (AA = amino acidate), where n = 2 and 0. The photochemical syntheses and chromatographic separation of diastereomers for the mixed-ligand complexes Cr(acac)$_2$(L), where acac is the anion of 2,4-pentanedione and L is the anion of (S)-alanine (S-ala), (S)-valine (S-val), or (S)-phenylalanine (S-phe), are described. CD spectra of the individual diastereomers are reported and compared with those of the nearest terminal member of the series (n = 3) and with the analogous Co(III) complexes. Isolation of two diastereomers of Cr(S-ala)$_3$ is described, CD spectra are shown, and the absolute configuration is assigned for one diastereomer.

Table I. Characterization of Chromium(III)–Amino Acidate Complexes

	% C	% H	% N	[M]$_{589}$
Cr(acac)$_2$(S-ala)				
Calcd	46.15	5.96	4.14	
Found, isomer A[d]	47.62	6.11	3.70	+21[a]
Found, isomer B	45.85	5.93	4.22	−230[a]
Cr(acac)$_2$(S-val)				
Calcd	49.18	6.60	3.83	
Found, isomer A	49.24	6.68	3.22	+1287[a]
Found, isomer B	49.25	6.64	3.47	−8522[a]
Cr(acac)$_2$(S-phe)				
Calcd	55.07	5.84	3.38	
Found, isomer A	54.87	5.76	3.52	+2136[a]
Found, isomer B	55.46	6.08	3.02	−4455[a]
Cr(S-ala)$_3$				
Calcd	34.18	5.74	13.29	
Found, isomer A	34.21	5.88	13.34	−186[b]
Cr(S-ala)$_3$·H$_2$O				
Calcd	32.33	6.03	12.57	
Found, isomer B	31.97	6.25	12.49	+78[c]

[a] Chloroform solution. [b] 20% H_2SO_4 solution. [c] Aqueous solution. [d] Crystals contain toluene (see Experimental Section).

Experimental Section

Syntheses. The mixed-ligand complexes Cr(acac)$_2$(S-α-AA) were prepared and separated into diastereomers by modifications of the procedures published earlier by Wingert, Seematter, and Brushmiller.[10] The following procedure proved successful for the amino acids S-ala, S-val, and S-phe.

A solution containing 3 mmol of Cr(acac)$_3$,[11] 4.5 mmol of amino acid, 4.0 mmol of NaOH, 10 ml of H$_2$O, and 90 ml of methanol was prepared. In order to keep the amino acid in solution, it was first dissolved in the water containing the NaOH; then this solution was added slowly to the methanol–Cr(acac)$_3$ solution. The resulting solution was distributed among several 1-cm diameter photolysis tubes which were then placed in a Rayonet RPR-100 photochemical reactor equipped with 8 RPR-3500 phosphor lamps (350 nm, bandwidth ~42 nm). Photolysis was carried out for 12 h, after which time all solvent was removed from the reaction mixture. The residue was taken up in a minimum of a 1:1 (v/v) mixture of acetone–CHCl$_3$ (where the amino acid was S-ala), a 1:9 (v/v) acetone–ethyl acetate mixture (for S-val), or a 1:9 (v/v) acetone–CHCl$_3$ mixture (for S-phe). After filtration to remove insoluble material, the solution in each case was introduced onto a 25-cm × 1 cm column of silica gel (Mallinckrodt SilicAR CC-7) and eluted with the same solvent. In each case a purple band containing unreacted Cr(acac)$_3$ was eluted first. This was followed by a red band which divided in two well-separated bands for S-ala and S-phe as it moved down the column. These bands did not separate completely for S-val, so only the first and last eluted portions were collected. An unidentified brown material remained at the top of the column, and other unidentified red and blue materials moved only slightly on the column. The two red products are the two diastereomers of Cr(acac)$_2$(S-AA). The first and second eluted isomers are designated A and B, respectively. After removal of solvent at reduced pressure from A and B, the complexes were recrystallized from toluene and n-heptane. Elemental analyses and molecular rotations obtained after drying in vacuo are given in Table I. Elemental analyses for Cr(acac)$_2$(S-ala)-A were consistently high in carbon and hydrogen. The presence of small amounts of toluene in the crystals was demonstrated by mass spectra of the complex below 100 °C, where the most intense peaks above background occur at m/e 92 and 91 (parent ion and parent − H). This toluene was not removed by heating (56 °C) the crystals in vacuo for 2–3 h. Heating at higher temperatures results in decomposition of the complex.

Co(acac)$_2$(S-phe) was prepared by Laurie's method.[12] The two diastereomers were separated by chromatographing the reaction mixture on a silica gel column as described above using a 2:3 (v/v) mixture of acetone–CHCl$_3$ as eluent.

Cr(S-ala)$_3$ was prepared by a modification of the method of Skinner and Jones.[13] In a typical preparation 6.0 g (0.067 mol) of (S)-alanine was dissolved in 15 ml of hot water. To this solution was added dropwise (with stirring) a solution of 4.0 g (0.015 mmol) of CrCl$_3$·6H$_2$O in 5 ml of water. The solution was then heated for 24 h, after which time 1.4 g (0.035 mol) of NaOH, dissolved in a minimum of water, was added dropwise. The color of the solution changed from blue-violet to red-violet, and a pink precipitate formed. The pH at this point was about 5. The solution was filtered immediately, and the precipitate was washed with 10 ml of water. This material contains two diastereomers of Cr(S-ala)$_3$ which differ considerably in their solubility in water. Extraction of the precipitate with several portions of water, totaling about 500 ml, separated the isomers. The pink, water-insoluble product, A, was obtained in 20% yield. The pink, water-soluble product, B, was recovered by removing solvent under reduced pressure. This must be done without delay due to the instability of the complex in aqueous solution. The yield for isomer B was ~15%. Elemental analyses, taken after drying of the products over P_2O_5 in vacuo, are given in Table I.

Co(S-ala)$_3$ was prepared by the method of Mori et al.[14] using $K_3[Co(CO_3)_3]$. A mixture of the pink Λ-cis and violet Λ-trans isomers precipitated during the preparative reaction. Cooling the reaction mixture caused more of the Λ-trans isomer to precipitate. This product mixture was extracted several times with hot water to separate the pink, water-insoluble Λ-cis isomer from the violet, slightly soluble Λ-trans isomer. These isomers were recrystallized from water (Λ-trans) or 50% H_2SO_4 (Λ-cis). To obtain the remaining two diastereomers, the solvent was removed under reduced pressure from the filtered reaction mixture, and the residue was taken up in a minimum amount of 1:1 (v/v) ethanol–water and applied to preparative-layer plates of silica gel (20 cm × 20 cm, 2-mm layer, Brinkmann F-254). Several elutions with a 10:9:1 (v/v) $CHCl_3$–ethanol–water solvent mixture effected separation. The faster moving band proved to be the Δ-trans diastereomer. Both Δ-trans and Δ-cis isomers were extracted from the silica gel with 1:1 (v/v) ethanol–water and recrystallized. The four diastereomers of Co(S-ala)$_3$ were identified by comparing their CD curves with those reported in the literature.[15]

Physical Measurements. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. CD and ORD spectra were obtained using a Cary Model 60 spectropolarimeter and accompanying Model 6001 CD accessory. X-ray powder diffraction data were obtained by the Debye–Scherrer technique using Ni-filtered Cu Kα radiation. The light quanta absorbed by the photolysis tubes under the experimental conditions employed was determined by routine ferric oxalate actinometry. Elemental analyses were made using a F & M Model 185 C, H, and N analyzer.

Results and Discussion

Synthesis of Mixed-Ligand Complexes, Cr(acac)$_2$(S-α-AA). Preliminary experiments confirmed the earlier report[10] that refluxing mixtures of Cr(acac)$_3$, amino acid, and base in methanol–water does not result in formation of the mixed-ligand species. However, irradiation of this solution with light at a number of wavelengths at ambient temperature causes ligand exchange of Cr(acac)$_3$. A recent mechanistic study[16] of the photoisomerization of a related Cr(β-dik)$_3$ complex indicates light serves to break a Cr–O bond, a process that occurs thermally to a significant extent only at temperatures over 100 °C. Initial quantum yields for formation of Cr(acac)$_2$(S-val) were measured at several wavelengths and were found to be 0.025 at 350 nm, 0.039 at 300 nm, and 0.042 at 254 nm. The most efficient wavelength for producing the maximum yield of product, despite its lower initial quantum yield, is 350 nm because it causes much less side product formation and decomposition. After several hours of photolysis at 254 and 300 nm, decomposition of the product competes effectively with product formation eventually resulting in a net decrease in the amount of product.

Two stereoisomers are possible for Cr(acac)$_2$(S-AA). These are designated Δ and Λ, where the symbols denote configuration about the pseudo-C_3 axis which corresponds to the C_3 axis of the parent complex, Cr(acac)$_3$. Since these are diastereomers, they may be separated by chromatography on an achiral sorbent such as silica gel. For each amino acid used the first-eluted isomer, A, was dextrorotatory at 589 nm. Isomers B were all levorotatory at this wavelength.

Absolute Configurations of Mixed-Ligands Complexes. In the previous paper in this series[3] it was shown that CD spectra of diastereomers of Co(acac)$_2$(S-AA) complexes closely resemble those of resolved tris(β-diketonato)cobalt(III) complexes for which Cotton effect–configuration relationships are known. The assumption was made that replacement of one acac by an amino acidate ligand causes only minor perturbation of the ligand field energy levels, and the Cotton effect–configuration rules known for the tris complex were applied to the mixed-ligand species. Configurational assignments made in this manner for Co(acac)$_2$(S-AA) diastereomers agreed in every case with assignments made independently from NMR anisotropy shielding studies.[17]

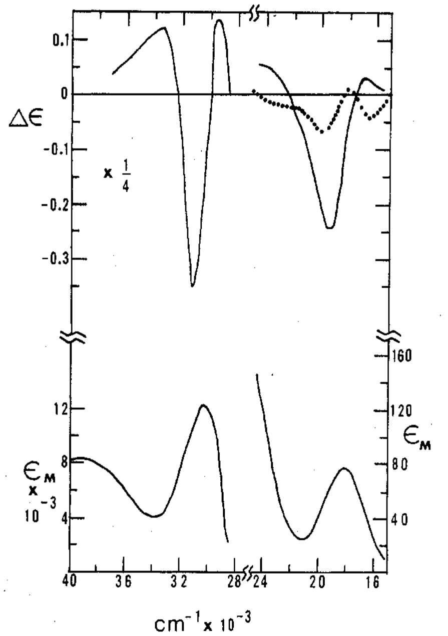

Figure 1. Absorption and CD spectra of Cr(acac)$_2$(S-ala) diastereomers in chloroform solution: · · ·, isomer A; —, isomer B.

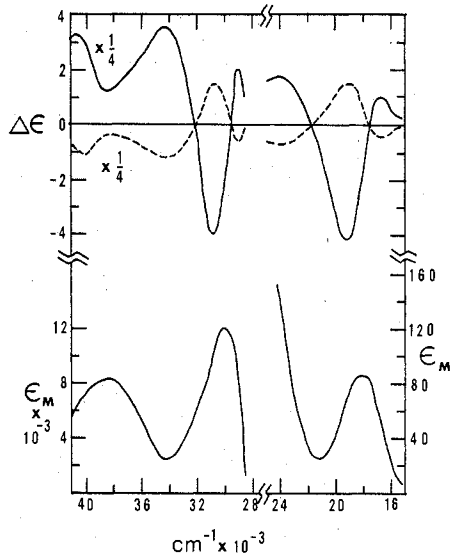

Figure 2. Absorption and CD spectra of Cr(acac)$_2$(S-val) diastereomers in chloroform solution: - - -, isomer A; —, isomer B.

Absorption and CD spectra of the Cr(acac)$_2$(S-AA) complexes are shown in Figures 1–3. Absorption spectra of diastereomers A and B in each case are virtually identical. The low-energy absorption band is attributed to a combination of low-symmetry components of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition in O_h symmetry. With the exception of isomer A of Cr(acac)$_2$(S-ala), CD bands associated with this transition consist of a dominant band followed by a much smaller band of opposite sign at lower energy. This same pattern of CD bands

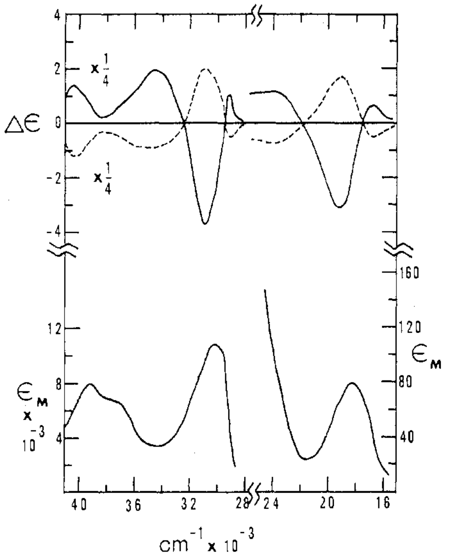

Figure 3. Absorption and CD spectra of $Cr(acac)_2(S\text{-phe})$ diastereomers in chloroform solution: - - -, isomer A; ——, isomer B.

is found for resolved $Cr(\beta\text{-dik})_3$ complexes.[4,18-22] Absolute configurations for the latter complexes may be assigned from the well-established[4,5,22] empirical rule that isomers for which the dominant, higher energy CD component of the visible transition is positive have the Λ configuration. Although the mixed-ligand species have only C_1 symmetry, it appears reasonable to assume here, as for the analogous Co(III) complexes, that deviations from the energy order of ligand field levels of $Cr(acac)_3$ are sufficiently small in the mixed-ligand species that the "parentage" arguments discussed earlier[3] may be applied. Accordingly, the $(+)_D$-$Cr(acac)_2(S\text{-AA})$ isomers (A) are assigned the Λ configuration, and the $(-)_D$ isomers (B) are assigned the Δ configuration.

These configurational assignments are supported by the following experiments. Using identical chromatographic conditions,[23] the relative rates of elution of $(+)_D$- and $(-)_D$-$Cr(acac)_2(S\text{-phe})$ were compared with those of $(+)_D$- and $(-)_D$-$Co(acac)_2(S\text{-phe})$. Since these pairs of complexes differ only in the metal ion, isomers having the same absolute configuration should be eluted at roughly the same rates. In each case the $(+)_D$-$M(acac)_2(S\text{-phe})$ isomers were eluted first, indicating they have the same configuration. $(+)_D$-$Co(acac)_2(S\text{-phe})$ is assigned the Λ configuration from the close similarity of its CD spectrum with those of other $Co(acac)_2(S\text{-AA})$ diastereomers assigned the Λ configuration.[3,17] This method of relating configurations of analogous Cr(III) and Co(III) complexes has been proven correct for tris complexes of the chiral β-diketone (+)-3-acetylcamphor.[4]

We have no explanation at present for the unexpected negative CD band at 20 000 cm^{-1} for $(+)_D$-$Cr(acac)_2(S\text{-ala})$. The component at lower energy has the expected sign and contour. Also it is not understood why all CD maxima for $Cr(acac)_2(S\text{-ala})$ are smaller by an order of magnitude than those of analogous complexes containing *S*-val and *S*-phe. The absorption spectra of all these complexes have similar intensities. The two diastereomers of $Cr(acac)_2(S\text{-ala})$ were well separated on the chromatographic column; thus it is believed they are optically pure.

These experiments were repeated with identical results. It is perhaps significant to note that CD band intensities for $Cr(S\text{-ala})_3$ are smaller by a factor of 4–5 than those of $Cr(S\text{-val})_3$.[24]

Comparison of CD Spectra of Cr(III) and Co(III) Complexes. In the C_3 point group the first spin-allowed transitions for d^3 and low-spin d^6 complexes belong to the same symmetry species, A and E. Thus if deviations from effective C_3 symmetry are small, Co(III) and Cr(III) complexes having identical ligands and identical configurations are both expected to have two CD bands of opposite sign in the region of the first spin-allowed transition.[6] Several publications from this laboratory have compared Cr(III) and Co(III) tris complexes believed to have identical configurations, and the expected CD similarities have been found.[4,25,26] A comparison of the CD spectra in Figures 1 and 2 with those of the corresponding Co(III) complexes published earlier[3] reveals that, with the exception of $(+)_D$-$Cr(acac)_2(S\text{-ala})$, spectra of diastereomers assigned identical configurations bear a close similarity with regard to number of peaks, relative amplitudes, and relative signs.

Table II. X-Ray Powder Diffraction Data for Tris(*S*-alaninato)cobalt(III) and -chromium(III) Complexes

Complex	Interplanar spacings, Å
Λ-*cis*-$Co(S\text{-ala})_3$[a]	10.81 vs, 8.56 w, 6.18 m, 5.41 vw, 4.53 s, 4.07 m, 3.90 m, 3.66 m, 3.60 m, 3.16 s, 2.91 m, 2.56 s, 2.50 w, 2.34 vw, 2.34 vw, 2.13 m
Isomer A of $Cr(S\text{-ala})_3$	10.77 vs, 8.53 w, 6.21 m, 5.37 vw, 4.56 s, 4.06 m, 3.91 m, 3.67 m, 3.57 m, 3.15 s, 2.90 m, 2.54 s, 2.50 w, 2.35 vw, 2.31 vw, 2.09 m
Isomer B of $Cr(S\text{-ala})_3 \cdot H_2O$	12.35 m, 11.47 m, 10.62 s, 9.30 vs, 8.76 m, 6.75 s, 5.08 w, 4.98 w, 4.66 w, 4.41 w, 4.29 s, 3.49 w, 2.78 s, 1.94 m, 1.56 m

[a] Absolute configuration assigned by Denning and Piper.[15]

Diastereomers of $Cr(S\text{-ala})_3$. The pink, water-insoluble isomer A of $Cr(S\text{-ala})_3$ is reminiscent of the pink, insoluble isomer of $Co(S\text{-ala})_3$, variously described as the cis-(+) or (+)-β isomer. Denning and Piper assigned the Λ-cis configuration to this isomer from a combination of NMR and CD studies.[15] Their configurational assignments for the four $Co(S\text{-ala})_3$ diastereomers were subsequently confirmed by Drew et al. from an x-ray diffraction study of the Λ-trans isomer.[27]

In an effort to relate configurations of the Cr(III) and Co(III) complexes, x-ray powder patterns of all four diastereomers of $Co(S\text{-ala})_3$ were made to compare with those of the two diastereomers of $Cr(S\text{-ala})_3$ isolated. Powder patterns among the four Co(III) diastereomers are quite different, but interplanar spacings for the Λ-cis isomer closely match those obtained for isomer A of $Cr(S\text{-ala})_3$ (see Table II). Thus, making the reasonable assumption that those diastereomers which are isomorphous have the same absolute configuration, isomer A of $Cr(S\text{-ala})_3$ is assigned the Λ-cis configuration. The powder pattern for isomer B does not match well with the powder pattern of any of the Co(III) diastereomers, and no conclusion can be drawn regarding the configuration of this isomer. CD spectra of the two $Cr(S\text{-ala})_3$ isomers suggest but do not prove that they have opposite helicities (Figure 4).

The two diastereomers of $Cr(S\text{-ala})_3$ reported here are not as stable in solution as the corresponding Co(III) diastereomers. Although the Λ-cis isomer seems stable for several hours in aqueous acid, isomer B decomposes rapidly in aqueous solution. Spectra of the latter must be recorded immediately after dissolving the solid, since a noticeable decrease in the CD maxima occurs within 15 min.

As discussed above for mixed-ligand complexes, it was anticipated that tris((*S*)-alaninate) complexes of Co(III) and Cr(III) having identical absolute configurations might have similar CD spectra. Visible absorption spectra shown in Figure 4 resemble those of the corresponding Co(III) complexes with regard to band shape and position; spectra of the Co(III)

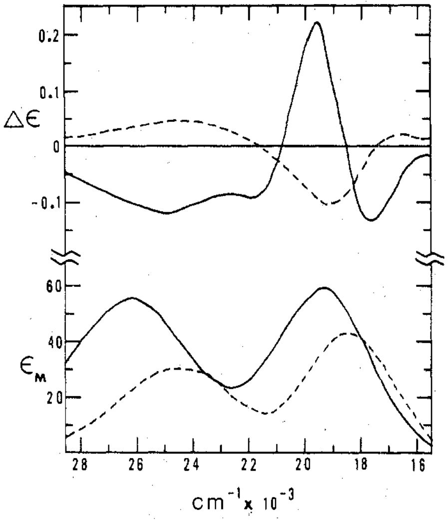

Figure 4. Absorption and CD spectra of two diastereomers of Cr(S-ala)$_3$: - - -, isomer A; ——, isomer B.

complexes are more intense by a factor of ~3. However CD spectra of Λ-*cis*-Cr(S-ala)$_3$ and Λ-*cis*-Co(S-ala)$_3$ in the region of the low-energy transition bear no obvious similarities. The dominant band for Λ-*cis*-Co(S-ala)$_3$ is positive,[15] whereas Λ-*cis*-Cr(S-ala)$_3$ shows a dominant negative band in this region (Figure 4). The CD spectrum of the latter resembles that reported earlier for the diastereomer of Cr(S-ala)$_3$ isolated by Vieles and Bonniol.[28]

In order for isostructural Co(III) and Cr(III) complexes to have similar CD spectra, the order of the ligand field energy levels (A and E in C_3 symmetry) must be the same for each ion. The absence of similarity in CD spectra of the tris(alaninato) complexes may indicate a change in relative energies of ligand field transitions on going from Co(III) to Cr(III). If this is the case, it would appear that the change does not occur until more than one amino acid is present, since CD spectra of isostructural complexes in the series M(β-dik)$_n$(S-AA)$_{3-n}$ for M = Cr(III) and Co(III) are quite similar for n = 3 and 2. A change in the order of ligand field energy levels may also be responsible for the opposite sign patterns observed in the long-wavelength CD spectra of tris(malonate) complexes of Co(III) and Cr(III) known to have identical configurations.[29] Another factor known to influence relative magnitudes of CD bands in Co(III) complexes containing optically active amino acidate ligands are "vicinal" effects of the ligands.[30] These effects combined with uncertainties in ordering of the ligand field energy levels preclude any attempt at present to derive reliable Cotton effect–configuration relationships for Cr(S-ala)$_3$ diastereomers

Acknowledgment. This work was supported by the Research Corp. and by the University of Kansas General Research Fund. We are indebted to Professor J.G. Brushmiller of the University of North Dakota for samples of some of the complexes examined.

Registry No. Cr(acac)$_2$(S-ala), isomer A, 55332-59-7; Cr(acac)$_2$(S-ala), isomer B, 55332-57-5; Cr(acac)$_2$(S-val), isomer A, 55332-58-6; Cr(acac)$_2$(S-val), isomer B, 55400-49-2; Cr(acac)$_2$(S-phe), isomer A, 59532-84-2; Cr(acac)$_2$(S-phe), isomer B, 59573-77-2; Cr(S-ala)$_3$, isomer A, 53833-75-3; Cr(S-ala)$_3$, isomer B, 59573-78-3; Cr(acac)$_3$, 21679-31-2; Λ-*cis*-Co(S-ala)$_3$, 15650-49-4.

References and Notes

(1) On exchange scholarship from the University of Hamburg, 1971–1972.
(2) C. J. Hawkins, "Absolute Configuration of Metal Complexes", Wiley-Interscience, New York, N.Y., 1971.
(3) G. W. Everett, Jr., K. S. Finney, J. G. Brushmiller, D. J. Seematter, and L. A. Wingert, *Inorg. Chem.*, **13**, 536 (1974).
(4) R. M. King and G. W. Everett, Jr., *Inorg. Chem.*, **10**, 1237 (1971).
(5) W. D. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Am. Chem. Soc.*, **92**, 7620 (1970).
(6) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).
(7) P. Anderson, F. Galsbol, and S. E. Harnung, *Acta Chem. Scand.*, **23**, 3027 (1969).
(8) S. Kaizaki, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **12**, 135, 142 (1973).
(9) H. Mizouchi, A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **44**, 1555 (1971), and references cited therein.
(10) L. A. Wingert, D. J. Seematter, and J. G. Brushmiller, *J. Chem. Soc., Chem. Commun.*, 976 (1974).
(11) W. C. Fernelius and J. E. Blanch, *Inorg. Synth.*, **5**, 130 (1957).
(12) S. H. Laurie, *Aust. J. Chem.*, **21**, 679 (1968).
(13) C. E. Skinner and M. M. Jones, *Inorg. Nucl. Chem. Lett.*, **3**, 185 (1967).
(14) M. Mori, M. Shibata, E. Kyuno, and M. Kanaya, *Bull. Chem. Soc. Jpn.*, **34**, 1837 (1961).
(15) R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).
(16) S. F. Minor and G. W. Everett, Jr., *Inorg. Chem.*, **15**, 1526 (1976).
(17) D. J. Seematter and J. G. Brushmiller, *J. Chem. Soc., Chem. Commun.*, 1277 (1972).
(18) K. L. Stevenson, *J. Am. Chem. Soc.*, **94**, 6652 (1972).
(19) K. L. Stevenson and T. P. vanden Driesche, *J. Am. Chem. Soc.*, **96**, 7964 (1974).
(20) H. Yoneda, Y. Nakashima, and U. Sakaguchi, *Chem. Lett.*, 1343 (1973).
(21) B. Norden, *Inorg. Nucl. Chem. Lett.*, **11**, 387 (1975).
(22) R. B. Von Dreele, C. J. Hinrichsen, and R. C. Fay, *Proc. Int. Conf. Coord. Chem.*, **16** (1974).
(23) A silica gel column such as described in the Experimental Section was used with a 2:3 (v/v) acetone–CHCl$_3$ mixture as the eluent.
(24) G. Witte and G. W. Everett, Jr., unpublished observations.
(25) J. E. Gray and G. W. Everett, *Inorg. Chem.*, **10**, 2087 (1971).
(26) K. S. Finney and G. W. Everett, Jr., *Inorg. Chim. Acta*, **11**, 185 (1974).
(27) M. G. B. Drew, J. H. Dunlop, R. D. Gillard, and D. Rogers, *Chem. Commun.*, 42 (1966).
(28) P. Vieles and A. Bonniol, *J. Chim. Phys. Phys.-Chim. Biol.*, **70**, 348 (1973).
(29) K. R. Butler and M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 251 (1976).
(30) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).