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Partial Resolution of Cobalt(III) Chelate Complexes by Ion-Exchange Cellulose Chromatography[1]

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The total resolution of the trinuclear cobalt(III) complex of 2-aminoethanethiol on cation-exchange cellulose has been reported.[3] Although total resolution of smaller mononuclear complexes does not appear feasible, this chromatographic method can be used to obtain partial resolution. Recently the resolution of a large nickel(II) macrocycle on microcrystalline cellulose and starch was reported.[4] Starch chromatography has also been used to obtain partial resolution of cobalt(III) complexes.[5,6]

Partial resolution of optical isomers on ion-exchange cellulose is convenient and appears to be generally applicable for the partial resolution of nonlabile chelate complexes. The method is rapid (several hours) and simple in operation (gravity flow with water as a solvent), and the cellulose in the columns appears to be stable over a period of several months. The method should serve as a diagnostic tool for the identification of isomers as well as permit the study of the optical activity of complexes which resist resolution. For example, changes in the circular dichroism (CD) patterns of a series of related complexes could be determined in 1 day when normally it might take several months to resolve the series of complexes if, indeed, resolving agents could be found. Such was the case for one of the newly resolved series reported below.

This method was used partially to resolve the complexes: *cis*-$Co(IDA)_2^-$ (IDA = iminodiacetate), $Co(TRDTA)^-$ (TRDTA = trimethylenediaminetetraacetate), $Co(EDTA)^-$, $CoA(en)^+$ (A = N,N′-dimethyl- and N,N′-diethylethylenediamine-N,N′-diacetate, DMEDDA and DEEDDA, respectively), and $Co(EDDA)B^+$ (B = N-methyl-, N-ethyl-, N,N′-dimethyl-, and N,N′-diethylethylenediamine, Men, Een, DMen, and DEen, respectively). Only the resolution of $Co(EDTA)^-$ has been previously reported.[7]

The degree of resolution achievable on one passage through the column is exemplified by the following data. The first fraction (3 ml) obtained from chromatography of $Co(EDTA)^-$ (2.0×10^{-3} *M*) had $\Delta\epsilon$ (582 mμ) = −0.88. The completely resolved isomer has $\Delta\epsilon$(582 mμ) = −1.50. Although the N-alkyl analogs of *trans*-$Co(EDDA)(en)^+$ have not as yet been completely resolved, the $\Delta\epsilon$ values obtained for these isomers, Figure 1, can be compared to $\Delta\epsilon = \pm 4.5$ (532 mμ) for the optical isomers of *trans*-$Co(EDDA)(en)^+$.[6] Larger first fractions (10–15 ml) were taken for these isomers.

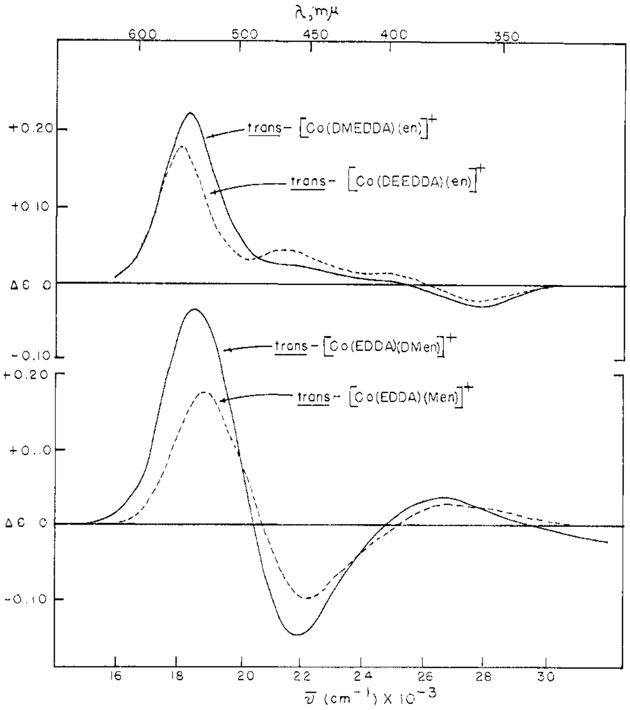

Figure 1.—The circular dichroism spectra obtained for $CoA(en)^+$ and $Co(EDDA)B^+$. (The CD spectra of the complexes B = Een and DEen are very similar to those of the N-methyl analogs.)

Some observations concerning the identity and circular dichroism (CD) spectra of the newly resolved complexes can be made. The CD data obtained for $Co(EDTA)^-$ and its analogs are recorded in Table I. Although the identities of the two facial isomers of $Co(IDA)_2^-$ have been established,[8] the partial resolution of the isomer presumed to be *cis* offers the classical proof of isomer assignment.

The *trans*[9] preference of EDDA and its N-alkyl analogs in these complexes is well established.[6,10]

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[3] G. R. Brubaker, J. I. Legg, and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 3446 (1966).

[4] L. T. Taylor and D. H. Busch, *ibid.*, **89**, 5372 (1967).

[5] H. Ley and H. Winkler, *Ber.*, **42**, 3900 (1909); **45**, 375 (1912); H. Krebs, J. Diewald, H. Arlitt, and J. A. Wagner, *Z. Anorg. Allgem. Chem.*, **287**, 98 (1956); B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

[6] J. I. Legg, D. W. Cooke, and B. E. Douglas, *ibid.*, **6**, 700 (1967).

[7] F. P. Dwyer and F. L. Garvan, *Inorg. Syn.*, **6**, 192 (1960).

[8] D. W. Cooke, *Inorg. Chem.*, **5**, 1141 (1966), and references therein.

[9] As used here and in previous reports, *trans* corresponds to α introduced for linear tetradentates by A. M. Sargeson and G. H. Searle, *ibid.*, **4**, 45 (1965).

[10] J. I. Legg and D. W. Cooke, *ibid.*, **4**, 1576 (1965).

TABLE I

CIRCULAR DICHROISM DATA OBTAINED FOR THE ANIONIC COMPLEXES

Complex	λ_1[a]	λ_2	λ_3	λ_4	λ_5
cis-$Co(IDA)_2^-$	582 (−)[b]	508 (+)		376 (−)[c]	
$Co(EDTA)^-$	579 (−)	504 (+)	419 (−)	385 (+)	361 (−)
$Co(TRDTA)^-$	578(−)	502 (+)	415 (−)[d]	382 (+)	361 (−)

[a] λ, mμ. [b] Sign of Δϵ. [c] Broad band. [d] Very weak.

This requires the configuration of the asymmetric nitrogens to be *RR* or *SS*[11] depending on the antimeric configuration of the tetradentate ligand, Figure 2.

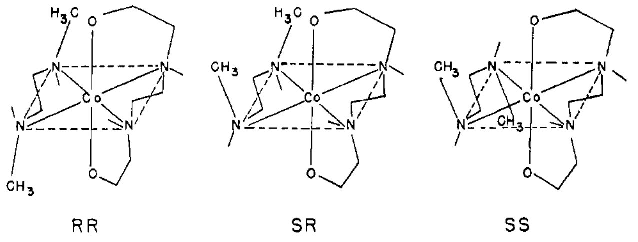

Figure 2.—The possible configurations for chelated DMEN. Chirality of the complex is $\Lambda(C_2)$ with the EDDA nitrogens in the *SS* configuration; see J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).

On the other hand, the configuration of the two N,N′-dialkyl-substituted nitrogens of DMen and DEen could be either *RR*, *SS*, or *RS*. For a given antimere, molecular models suggest that the *meso* form will lie intermediate in energy between *RR* and *SS*. The N-alkyl substituents are much more sterically crowded when projected on the face containing one of the EDDA acetate arms, *RR* in Figure 2.

When the diamine is in the *RR* or *SS* conformation, the complex possesses a C_2 axis. Proton nmr of these two complexes showed only one type of methyl (a singlet for the DMen and a triplet for the DEen complexes) as well as only one AB pattern for the two acetate arms of EDDA, confirming the observation made with models. Although coincidence of signals is possible, it is improbable that there would be coincidence of both the methyl signals and the AB patterns. In fact, nmr chemical shifts proved to be very sensitive in an analogous situation where the diastereoisomers of $Co(EDDA)(l\text{-pn})^+$ were distinguished by the splitting of the AB pattern in the isomer where nonbonding interactions were the greatest.[6] Stereoselectivity associated with an asymmetric nitrogen in cobalt(III) complexes has been observed by others.[12]

The circular dichroism spectra of the EDDA family of complexes are given in Figure 1. If it is assumed that the sign of the low-energy component (−18,600 cm^{-1}) reflects the absolute configuration of these complexes,[6] then placing the N-alkyl substituents on the tetradentate ligand has the effect of changing the sign of the higher energy B component (~22,000 cm^{-1}). This electronic transition is not expected to be related to the absolute configuration of the complex.[13] Even then it is somewhat surprising that what would appear to be a small difference between two complexes (*e.g.*, shifting the two N-methyl groups from ethylenediamine to EDDA) with the same absolute configuration leads to a significant change in the CD spectrum and emphasizes the importance of asymmetric nitrogen centers.

Experimental Section

Preparation of Complexes.—The complexes *trans*-[Co(EDDA)-B]NO_3 were prepared by a method analogous to that previously reported for the complexes *trans*-[CoA(en)]NO_3.[10] The analyses are recorded in Table II. The complexes where B = DMen and DEen were converted to the more soluble chloride salts for the proton nmr spectra by ion exchange. Previously reported procedures were used to prepare *cis*-K[Co(IDA)$_2$],[14] K[Co-(TRDTA)],[15] and K[Co(EDTA)].[16]

Chromatography of Complexes.—About 20 g of Cellex-CM cation-exchange cellulose in the sodium form (Bio-Rad Laboratories) was stirred with 400 ml of 0.01 *M* $NaClO_4$. After allowing the cellulose to settle for 30 min, the supernate was decanted and the process was repeated. After adding 100 ml of 0.01 *M* $NaClO_4$, the mixture was rapidly stirred and immediately poured continuously into a column (diameter 2.5 cm, height 50–70 cm). The cellulose was allowed to settle for about 30 min and a plug of glass wool was inserted to protect the surface. (The cellulose bed should be continuous or the flow of eluent may be greatly restricted.) First 100 ml of 0.01 *M* $NaClO_4$ and then 100 ml of water were passed through the column at full flow rate (2–4 ml/min).

TABLE II

CHEMICAL ANALYSES OBTAINED FOR THE NEW COMPLEXES

Complex	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
Men, $[CoC_9H_{20}N_4O_4]NO_3$	29.27	29.17	5.46	5.38	18.97	19.10
Een, $[CoC_{10}H_{22}N_4O_4]NO_3$	31.34	30.91	5.79	5.80	18.28	18.32
DMen, $[CoC_{10}H_{22}N_4O_4]NO_3\cdot0.5H_2O$	30.62	30.86	5.91	5.87	17.86	18.05
DEen, $[CoC_{12}H_{26}N_4O_4]NO_3\cdot H_2O$	33.57	33.49	6.58	6.50	16.31	16.51

From 0.2 to 0.3 g of complex to be chromatographed was dissolved in 100 ml of water and loaded onto the column (1–2 ml/min). The 3–4-cm layer was then eluted over a period of 3 hr (longer periods did not seem to improve the resolution) with 0.01 *M* $NaClO_4$. The complex was collected in 10–15 15-ml fractions which were either evaporated down or used directly to obtain circular dichroism spectra.

Cellex-AE anion-exchange cellulose was used for the anionic complexes. The cellulose (40 g) was equilibrated with 0.02 *M* NaCl as described for the cation cellulose and the complex (0.2

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[11] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

[12] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, **6**, 1032 (1967), and references therein; H. G. Hamilton, Jr., and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).

[13] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

[14] J. Hidaka, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

[15] N. Tanaka and H. Ogino, *ibid.*, **37**, 877 (1964).

[16] F. P. Dwyer, E. C. Gyarfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

g) was eluted with 0.01 *M* NaCl. The initial fractions taken were about 3 ml each.

Spectra.—The circular dichroism (CD) spectra were recorded on a Roussel–Jouan Dichrographe and a Jasco Model ORD–UV-5 with CD attachment. Concentrations of the solutions (10^{-3}–10^{-2} *M*) were determined through their absorption spectra recorded on a Cary Model 14 spectrophotometer. The proton nmr spectra were obtained in D_2O on a Varian A-60 spectrometer.

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Preparation and Properties of Metal(II) Complexes of N-Methylformamide

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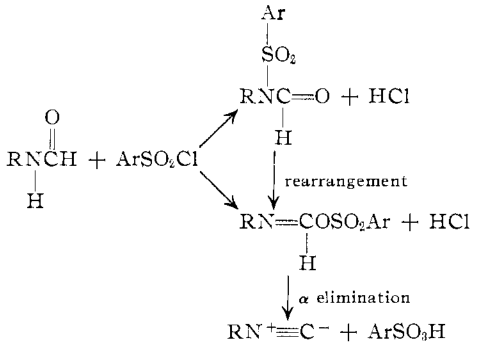
In a recent review Ugi, *et al.*,[1] describe experiments in which N-alkylformamides are dehydrated easily by various electrophiles, including arylsulfonyl chlorides, to produce isocyanides. The probable mechansim of this reaction involves electrophilic attack at formamide oxygen (eq 1b).[1] However, initial attack at formamide nitrogen (eq 1a) followed by rapid rearrangement has not been eliminated. In fact, reaction of various alkylformamides with acetyl chloride leads to stable N-acetylated derivatives.[2]



$$\mathrm{RN(H)CH{=}O} + \mathrm{ArSO_2Cl} \rightarrow \mathrm{RN(SO_2Ar)C(H){=}O} + \mathrm{HCl} \quad (1a)$$

$$\mathrm{RN(H)CH{=}O} + \mathrm{ArSO_2Cl} \rightarrow \mathrm{RN{=}C(H)OSO_2Ar} + \mathrm{HCl} \quad (1b)$$

$$\mathrm{RN{=}C(H)OSO_2Ar} \xrightarrow{\alpha\ \text{elimination}} \mathrm{RN^{+}{\equiv}C^{-}} + \mathrm{ArSO_3H} \quad (2)$$

We have undertaken a study of the effect of metal ion complexation on the reactivity of N-substituted formamides. We report here the preparation and chemical and physical properties of a series of N-methylformamide (NMF) complexes. The colors, methods of preparation, and analytical results are listed in Table I. A number of physical properties, including carbonyl stretching frequencies, magnetic moments, and molar conductances, are presented in Table II. The electronic absorption spectra are given in Table III. None of the perchlorate complexes on treatment with *p*-toluenesulfonyl chloride (TsCl) in nitromethane produced isocyanide, whereas NMF itself did. The nitrate complexes in nitromethane gave a weak isocyanide test. The complexes are generally soluble in highly polar solvents (*e.g.*, CH_3NO_2, alcohols, NMF) and insoluble in less polar solvents (*e.g.*, $CHCl_3$, CH_2Cl_2, ether, ethyl acetate). The complexes hydrolyze in water. Though the preparation and physical properties of a number of metal–amide complexes have been described,[3-6] we do not believe that there has been any comprehensive study of the metal complexes of N-monosubstituted formamides.

Physical Properties.—The shift of the C=O stretching band to lower frequency (relative to NMF) indicates that the formamide is coordinated to the metal *through the oxygen atom*, although the shifts (~10–20 cm^{-1}) are less than those usually found for metal–amide complexes (~30–70 cm^{-1}).[3,5] The electronic spectra of the Co and Ni complexes (Table III) in NMF and CH_3NO_2 are characteristic of the high-spin octahedral complexes, and their magnetic moments (Table II) are within the ranges observed for these complexes. The ligand field parameters were calculated using the matrix elements given by Orgel.[7] The calculated and observed values of ν_2 are in good agreement, substantiating the assignment of octahedral configuration for Ni and Co (Table IV).

The observed value for Ni given in Table IV is the average of the two maxima in the doublet. The value of *Dq* for the nickel perchlorate salt in NMF is in good agreement with that obtained by Drago, *et al.*[4] (838 cm^{-1}). However, it is evident from the data in Table IV that the value of *Dq* is somewhat dependent on both the solvent and the anion. For the $Ni(NMF)_6^{2+}$ species (ClO_4^- or NO_3^- anion, NMF and CH_3NO_2 as solvent) the value of *Dq* ranges from 840 to 859 cm^{-1}.

The electronic spectrum of $[Cu(NMF)_4](ClO_4)_2$, for both the solid (Nujol mull) and the NMF solution, consists of a broad band at 14,000 cm^{-1} which probably contains two or more overlapping bands. The ratio of the principal ligand field band of Cu to that of Ni (σ_{Cu}/σ_{Ni}) is 1.67, indicating a highly tetragonal complex.[8] The ir spectrum (4000–250 cm^{-1}) of the solid shows no evidence for coordinated perchlorate (*i.e.*, no splitting of ν_3 or ν_4 and a weak ν_1). However, the high melting point of the Cu complex (210–211° dec) would tend to indicate a stronger interaction between the anion and cation than in the $[M(NMF)_6](ClO_4)_2$ complexes. In any event, it is clear that the $Cu(NMF)_4^{2+}$ moiety is square planar rather than pseudo-tetrahedral.[9]

The stoichiometry, the similarity of melting points, and the presence of only one C=O stretching band in-

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[1] I. Ugi, U. Fetzer, H. Knupfer, and K. Offerman, *Angew. Chem. Intern. Ed., Engl.*, **4**, 472 (1965).

[2] D. J. Hoy and E. J. Poziomek, unpublished results.

[3] W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963).

[4] R. S. Drago, D. W. Meek, M. D. Joesten, and L. La Roche, *ibid.*, **2**, 124 (1963).

[5] S. K. Madan, *ibid.*, **6**, 421 (1967).

[6] S. K. Madan and J. A. Sturr, *J. Inorg. Nucl. Chem.*, **29**, 1669 (1967).

[7] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

[8] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Papers, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962, p 124.

[9] R. D. Willett, O. L. Lites, Jr., and C. Michelson, *Inorg. Chem.*, **6**, 1885 (1967).