quantities of acetylene, while the germanium analogue does not. These results point out the enhanced reactivity and diminished stability of the tin polymer over the germanium analogue.

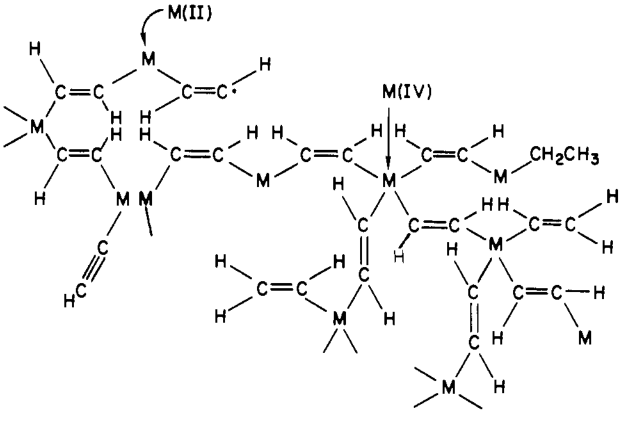
Discussion

It is clear that the cocondensations of germanium or tin atoms with acetylene produce air-sensitive, polymeric products of reproducible stoichiometry, i.e., $(C_2H_{2.7}Ge_{0.72})_x$ and $(C_2H_{2.6}Sn_{0.70})_x$. The compounds are weakly paramagnetic, with about one unpaired electron for every 20 000 and 3 500 000 carbon atoms, respectively. They react with oxygen irreversibly, and the oxidized polymers no longer exhibit an ESR spectrum. Mössbauer spectra indicate that the tin–acetylene polymer contains both tin(II) and tin(IV) species but that no α-tin, β-tin, or SnO_2 is present before exposure to air.

The pressed-powder conductivities of the polymers are very low, indicating that although germanium and tin atoms do react with acetylene to form a polymer, doping to the semiconducting or metallic state does not occur.

Thermal decomposition studies indicate that the tin–acetylene polymer is less thermally stable than the germanium analogue. This parallels the air sensitivity of the two polymers. Peaks in the mass spectra corresponding to acetylene, ethylene, butadiene, butenes, benzene, and residual toluene solvent have been identified.

Taking these data together, the best average structure for these polymers may be



high polymer, cross-linked, with occasional defects, resulting in trapped radicals; note C_2H, C_2H_3, and C_2H_5 units

With regard to the unique nature of Ge and Sn atoms for these copolymerization reactions, we have investigated many other metals such as V, Cr, Mn, Fe, Co, Ni, Pb, and others. Only Ge and Sn yielded these polymeric materials. The electronic configurations of the ground-state atoms as ^3P diradical species may account for this uniqueness.[24] A possible reaction mode is shown in Scheme I. We carried out a Ge vapor/$HC\equiv CH$ deposition at 10 K under matrix-isolation conditions[25] and observed no changes using infrared as a probe.[26] We hope to extend these studies to ESR soon.

Acknowledgment. We thank J. J. Zuckerman and T. S. Dory for Mössbauer studies, A. G. MacDiarmid and S. Porter for conductivity studies, M. B. Jones for ESR assistance, A. S. Eriksson for technical assistance, and the Phillips Petroleum Co. Foundation for a fellowship for R.W.Z. The support of the National Science Foundation is acknowledged with gratitude.

Registry No. Germanium, 7440-56-4; tin, 7440-31-5; acetylene, 74-86-2.

Supplementary Material Available: Listings giving germanium vaporized vs. acetylene consumed (Table V), tin vaporized vs. acetylene consumed (Table VI), and infrared absorptions for the metal–acetylene polymers (Table VII), ESR spectrum of the Ge–acetylene polymer (Figure 3), and Mössbauer spectra of Sn–acetylene polymers (Figures 4–6) (7 pages). Ordering information is given on any current masthead page.

---

(24) For earlier studies of Ge atom chemistry see: McGlinchey, M. J.; Tan, T. S. *Inorg. Chem.* **1975**, *14*, 1209.

(25) For matrix-isolation studies of acetylene with Al atoms see: Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1977**, *99*, 3521. Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 1165. With Ni atoms see: Ozin, G. A.; McIntosh, D. F.; Power, W. J.; Messmer, R. P. *Inorg. Chem.* **1981**, *20*, 1782. With Li/Na atoms see: Hauge, R. H.; Krishnan, C. N.; Margrave, J. L. "Abstracts of Papers", 170th National Meeting of the American Chemical Society, Chicago, IL, 1975; American Chemical Society: Washington, DC, 1975; INOR 95. Kasai, P. H. *J. Phys. Chem.* **1982**, *86*, 4092.

(26) Pure acetylene is a poor matrix material for low-temperature matrix-isolation infrared studies, due to very strong and broad infrared absorptions for the uncomplexed acetylene molecules, the tendency for acetylene molecules to self-cluster in matrices, and the large matrix site splitting seen in pure acetylene matrices: Hauge, R. H., personal communication.

Notes

Contribution from the Department of Chemistry,
Western Washington University, Bellingham, Washington 98225

Synthesis and Characterization Studies on New Ethylenediamine-*N*,*N*-diacetate Complexes of Cobalt(III)[1]

Gary A. Sigel and John A. Weyh*

Received October 12, 1983

Numerous complexes[2] of the sort $[Co(EDDA)(L)]^{\pm}$ (EDDA = ethylenediamine-*N*,*N'*-diacetate ion (symmetrical EDDA)), where L = CO_3^{2-}, ox, mal, and en, and $[Co(EDDA)(X)_2]^{\pm}$, where X = Cl^-, NO_2^-, and H_2O, have been thoroughly studied by Legg et al.[3] and Garnett and Watts.[4] Both s-cis and uns-cis isomers were obtained and characterized by using ion-exchange, NMR, and UV–vis techniques; s-cis (symmetrical cis) and uns-cis (unsymmetrical cis) describe geometrical configurations for EDDA. In each case the two coordination positions not occupied by EDDA are cis to one other. In the s-cis configuration the two EDDA acetate arms are trans, while in uns-cis the acetate arms are cis.[5] By

---

(1) Reported at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 20–25, 1983. Taken in part from: Sigel, G. A. M.S. Thesis, Western Washington University, 1982.

(2) Abbreviations: U-EDDA = ethylenediamine-*N*,*N*-diacetate, EDDA = ethylenediamine-*N*,*N'*-diacetate, ox = oxalate, mal = malonate, en = ethylenediamine, tn = 1,3-propanediamine (trimethylenediamine).

(3) Coleman, P. F.; Legg, J. I.; Steele, J. *Inorg. Chem.* **1970**, *9*, 937.

(4) Garnett, P. J.; Watts, D. W. *Inorg. Chim. Acta* **1974**, *8*, 293.

0020-1669/84/1323-3246$01.50/0

contrast, the related system $[Co(U\text{-}EDDA)(L)]^{\pm}$, where U-EDDA = unsymmetrical EDDA = ethylenediamine-*N*,*N*-diacetate, has been studied sparingly and only with N bonding ligands. Only two geometrical configurations are possible for U-EDDA. The two acetate arms are either trans or cis with respect to one another. Cooke et al.[6] have prepared cis- and trans-$[Co(U\text{-}EDDA)(en)]Cl$, and Kuroda et al.[7] have prepared trans isomers only for $[Co(U\text{-}EDDA)(L)]^{+}$, where L = en, tn, and $(NH_3)_2$. Cooke utilized ion-exchange, NMR, and UV–vis characterization techniques whereas Kuroda used only UV–vis. We wish to report synthesis and characterization studies on the $[Co(U\text{-}EDDA)(L)]^{\pm}$ system, where L = CO_3^{2-}, ox, mal, and tn (tn = $H_2N(CH_2)_3NH_2$).

Experimental Section

Synthesis of Ethylenediamine-*N*,*N*-diacetic Acid (H_2U-EDDA). The method reported by Martell et al.[8] was used except that the precipitation procedure was modified as described. The ligand solution was neutralized to pH 4 with 12 M HCl, and the volume was adjusted to 190–200 mL. A 3-fold or greater volume of absolute EtOH (600 mL) was added with rapid stirring. A milky oil was formed at the bottom of the beaker and was separated from the aqueous EtOH by decantation. Approximately 200 mL of absolute EtOH (one-third of the above volume) was added to the oil, and the mixture was stirred, warmed, and stirred. Gradually the oil thickened and finally solidified (total time to solidification 20 min). The crude material was then filtered and recrystallized as described.

Synthesis of *cis*-K[Co(U-EDDA)(CO_3)]·H_2O. $Na_3[Co(CO_3)_3]\cdot 3H_2O$ was prepared as described by Bauer and Drinkard.[9] $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (11.7 g, 0.032 mol) and H_2U-EDDA (5.5 g, 0.031 mol) were dissolved in 20 mL of H_2O, and the mixture was heated to 50 °C with stirring for 15 min. The solution was filtered, and addition of 95% EtOH to the purple filtrate produced a purple tar. The liquid was decanted, 50 mL of EtOH was added, and on trituration purple crystals appeared. A 1.0-g sample of the crude product was dissolved in 10 mL of H_2O, and the solution was charged onto a Bio-Rad AG 1-X8 anion-exchange column in the acetate form. Elution was accomplished with 0.2 M KOAc. Only one band with 1– charge characteristics was present. This band was collected and evaporated in vacuo at 50 °C nearly to dryness. To the completely dissolved material were added 3 mL of H_2O and 3 mL of absolute EtOH, and crystallization occurred overnight in a refrigerator. The product was filtered, washed with cold EtOH/H_2O solution (3:2 volume ratio), and dried at 65 °C for 2 h. NMR established the material as the cis isomer. Anal. Calcd for *cis*-K[Co(U-EDDA)(CO_3)]·H_2O: C, 24.00; H, 3.45; N, 7.99. Found: C, 23.94; H, 3.35; N, 7.81.

Synthesis and Separation of *cis*- and *trans*-K[Co(U-EDDA)(mal)]. $CoCO_3$ (1.08 g, 9.1×10^{-3} mol) and H_2U-EDDA (1.60 g, 9.1×10^{-3} mol) were mixed in 15 mL of H_2O, and the solution was stirred and heated to 80 °C for 15 min. After filtering, 10 mL of solution containing H_2mal (0.646 g, 6.2×10^{-3} mol) and Na_2mal·H_2O (0.50 g, 3.0×10^{-3} mol) was added to the filtrate, followed by 1 mL of 30% H_2O_2. The solution was heated to 85 °C, stirred for 15 min, and then charged onto a Bio-Rad AG 1-X8 column in the acetate form. The column was washed with H_2O to remove uncharged and 1+ charged species. The desired material was removed from the column by elution with 0.1 M KOAc. No separation was achieved on the column. Separation of the isomers was accomplished by fractional crystallization. The solution was evaporated to dryness and 2 mL of H_2O added. Upon addition of 30 mL of absolute EtOH, a purple solid precipitated and continued to precipitate overnight in a refrigerator. Filtration of the solid yielded a purple mud, and the filtrate, which contained mainly dissolved KOAc, was discarded. Ten milliliters of H_2O was added to the solid, which then dissolved at 60 °C. After dissolution and with continued stirring and heating, absolute EtOH (6 mL) was added dropwise until a slight cloudiness occurred. When the mixture was cooled in a refrigerator, reddish crystals began to form and continued to form overnight. The crystalline product was filtered out, washed with cold 2:1 EtOH/H_2O, and dried at 65 °C for 2 h. Recrystallization was accomplished by dissolving the solid in a minimum amount of H_2O, adding an equal volume of EtOH, and cooling. NMR and UV–vis spectra clearly established this as the cis isomer.

The remaining filtrate was evaporated to dryness and 3 mL of H_2O added to dissolve the solid. After filtration, addition of 50 mL of absolute EtOH caused precipitation of large clumps of purple material. The solid was filtered and redissolved in 0.5 mL of H_2O. Absolute EtOH (6 mL) was added dropwise with stirring and heating (70 °C) until purple crystals began to appear. While still warm, this material was filtered and dried at 65 °C. Recrystallization was accomplished by dissolving the solid in a minimum amount of H_2O, adding an equal amount of EtOH, and allowing crystallization to occur overnight in a refrigerator. Beautiful purple crystals were obtained and dried at 60 °C for 2 h. NMR and UV–vis spectra clearly established this as the trans isomer. Anal. Calcd for *cis*-K[Co(U-EDDA)(mal)]·1.25H_2O: C, 27.25; H, 3.68; N, 7.06. Found: C, 27.19; H, 3.63; N, 7.09. Calcd for *trans*-K[Co(U-EDDA)(mal)]·2H_2O: C, 26.35; H, 3.93; N, 6.83. Found: C, 26.23; H, 3.96; N, 6.79.

Synthesis and Separation of *cis*- and *trans*-K[Co(U-EDDA)(ox)]. Crude *cis*-K[Co(U-EDDA)(CO_3)]·H_2O (2.0 g, 5.8×10^{-3} mol) was dissolved in 20 mL of H_2O. Oxalic acid (0.86 g, 6.8×10^{-3} mol) was dissovled in 10 mL of warm H_2O. The two solutions were mixed and heated to 55 °C for 2 h. CO_2 was evolved initially. The solution was filtered and charged onto a Bio-Rad AG 1-X8 column in the acetate form. Elution with 0.1 M KOAc produced only one reddish purple band, which was evaporated in vacuo (55 °C) nearly to dryness. To the residue was added 1 mL of H_2O, and absolute EtOH (6 mL) was added dropwise with heating (55 °C) and stirring until a trace of cloudiness persisted. Crystallization occurred overnight in a refrigerator. Filtration showed the presence of both reddish and purple crystals, with red considerably more prevalent than purple. The solid mixture was dissolved in 0.5 mL H_2O, and absolute EtOH (2 mL) was added dropwise with warming and stirring. Crystallization occurred overnight in a refrigerator. Pure red crystals were obtained by filtration, washed with cold 3:2 EtOH/H_2O, and dried at 60 °C for 2 h. NMR and UV–vis spectra clearly established this as the cis isomer.

A small amount of an impure purple solid was isolated from the above filtrate. Preliminary UV–vis and NMR spectra would suggest that this is the trans isomer. The samples we obtained are small, extremely hygroscopic, and quite impure by analysis. Work is continuing on complete characterization of this material.

The cis isomer was also prepared from $CoCO_3$ as starting material in a manner similar to that described for the malonate complex. The *cis*-K[Co(U-EDDA)(ox)] complex obtained was identical with that described above.

With *cis*-K[Co(U-EDDA)(CO_3)]·H_2O as starting material the following analysis was obtained. Anal. Calcd for *cis*-K[Co(U-EDDA)(ox)]·H_2O: C, 25.40; H, 3.19; N, 7.41. Found: C, 25.29; H, 3.00; N, 7.50.

Synthesis and Separation of *cis*- and *trans*-[Co(U-EDDA)(tn)]Cl. Crude *cis*-K[Co(U-EDDA)(CO_3)]·H_2O (2.4 g, 6.8×10^{-3} mol) was dissolved in 10 mL of H_2O, 4.5 mL of 3 M HCl was added dropwise, and the solution was heated to 60 °C for 25 min. An aqueous solution containing 6.8×10^{-3} mol of tn was added and the mixture heated for 2 h at 60 °C. The solution changed from purple to red during this time. After cooling to room temperature, the solution was charged onto a Bio-Rad AG 50W-X8, 100–200 mesh cation-exchange column in the H^+ form. Elution was accomplished with 0.6 M HCl. Three 1+ charge bands developed. The first was purple and very faint and most probably was the diaquo species. The second and third bands were red and represented, by far, the majority species in solution. At the top of the column, remaining unmoved, was a small orange band. The second and third bands, assigned as *trans*- and *cis*-$[Co(U\text{-}EDDA)(tn)]^{+}$, respectively, were easily separated on the column. Preliminary geometric assignments were based on expected isomer polarities. After the trans band had been collected, the orange top layer of resin was removed by suction and the cis isomer then eluted with 1.0 M HCl.

Solid trans complex was obtained by mixing the trans solution with a 10% excess of a slurry of Bio-Rad 2-X8, 100–200 mesh resin in the OH^- form. After filtration, the filtrate was passed through a small

---

(5) Brubaker, G. R.; Schaefer, D. P.; Worrell, J. H.; Legg, J. I. *Coord. Chem. Rev.* **1971**, *7*, 161.

(6) Chu, M. W. S.; Cooke, D. W.; Liu, C. F. *Inorg. Chem.* **1968**, *7*, 2453.

(7) Kuroda, K.; Ohtsuka, S.; Matsumoto, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1055.

(8) McLendon, G.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1975**, *14*, 1993.

(9) Bauer, H. F.; Drinkard, W. C. *Inorg. Synth.* **1966**, *8*, 202.

Table I. Resonance Frequency Assignments and Integration Values for NMR Spectra

	$>NCH_2CO_2^-$ (R_2)	no. of H's	$>NCH_2CO_2^-$ (G_2)	no. of H's	$>N(CH_2)_nN<$ (n = 2 and/or 3)	no. of H's
trans-[Co(U-EDDA)(tn)]$^+$	4.73, 4.45, 4.11, 3.82[a]	4.0			3.5–2.0[a]	10.2
trans-[Co(U-EDDA)(mal)]$^-$	4.68, 4.40, 3.92, 3.65	4.0			3.4–2.7	3.8
cis-[Co(U-EDDA)(tn)]$^+$	4.15	4.0[b]	4.68, 4.39, 4.16, 3.87	4.0[b]	3.6–1.9	9.8
cis-[Co(U-EDDA)(CO_3)]$^-$	3.88	2.0	4.31, 4.10, 4.03, 3.78	2.0	3.5–2.7	4.2
cis-[Co(U-EDDA)(mal)]$^-$	3.98	2.1	4.35, 4.08, 3.75, 3.50	2.2	3.4–2.8	3.8
cis-[Co(U-EDDA)(ox)]$^-$	4.02	2.2	4.48, 4.22, 3.94, 3.68	2.1	3.5–2.9	4.1

[a] Units of δ. [b] Total $R_2 + G_2$.

Table II. Glycinate Ring Methylene Proton Resonance Line Assignments

	G_2 ring			R_2 ring		
complex	H_A	H_B	$\Delta\delta$[b]	H_A	H_B	$\Delta\delta$[b]
trans-[Co(U-EDDA)(tn)]$^+$				4.55[a]	4.00	0.55
trans-[Co(U-EDDA)(mal)]$^-$				4.51	3.81	0.70
cis-[Co(U-EDDA)(tn)]$^+$	4.49[a]	4.06	0.43	4.15		
cis-[Co(U-EDDA)(CO_3)]$^-$	4.16	3.97	0.19	3.88		
cis-[Co(U-EDDA)(mal)]$^-$	4.18	3.65	0.53	3.98		
cis-[Co(U-EDDA)(ox)]$^-$	4.32	3.84	0.48	4.02		

[a] Units of δ. [b] Difference in chemical shifts given by the formula $\delta_A - \delta_B = [(\delta_1 - \delta_4)(\delta_2 - \delta_3)]^{1/2}$.

column of Bio-Rad 2-X8 resin in the Cl^- form to remove any OH^-. After being mixed with the OH^- resin, the filtrate never exhibited a pH >6–7. Vacuum evaporation (40 °C) of this solution to 10 mL followed by the addition of absolute EtOH and placement in a freezer for 48 h produced a beautiful red crystalline product. The solid was recrystallized from a concentrated aqueous solution or, alternatively, by dissolving the solid in a minimum amount of H_2O, adding absolute EtOH until a trace of cloudiness persisted, and then cooling overnight in a refrigerator. The recrystallized material was washed with cold, aqueous EtOH and dried at 80 °C for 1 h. NMR and UV–vis spectra confirmed the trans geometry.

Solid cis complex was obtained by using a procedure essentially identical with that outlined for the trans isomer. The cis complex crystallized more readily from concentrated aqueous solution than did the trans. NMR and UV–vis spectra confirmed the initial cis assignment. Anal. Calcd for *trans*-[Co(U-EDDA)(tn)]Cl·H_2O: C, 29.97; H, 6.15; N, 15.53. Found: C, 30.12; H, 5.97; N, 15.42. Calcd for *cis*-[Co(U-EDDA)(tn)]Cl·1.5H_2O: C, 29.24; H, 6.27; N, 15.15. Found: C, 29.18; H, 5.94; N, 14.95.

Physical Measurements. Proton nuclear magnetic resonance spectra were recorded on a Varian T-60 NMR spectrometer. Deuterium oxide was used as solvent with sodium 4,4-dimethyl-4-silapentane-1-sulfonate (NaDSS) as an internal reference. The visible absorption spectra were recorded on a Cary Model 14 spectrophotometer. Analyses were performed by Canadian Microanalytical Service, Ltd., or Mic Anal.

Results and Discussion

Separation of Isomers. The s-cis and uns-cis isomers in the [Co(EDDA)(L)]$^\pm$ and [Co(EDDA)$(X)_2$]$^\pm$ series, where L = CO_3^{2-}, ox, mal, and en and X = Cl^-, NO_2^-, and H_2O, have been easily separated by using ion-exchange chromatography.[3,4] For the [Co(U-EDDA)(L)]$^+$ complexes studied to date (L = en or tn), both cis and trans isomers were easily separated by using Dowex or Bio-Rad AG 50W-X8, 100–200 mesh resin. Separation of cis and trans isomers of the anionic complexes of [Co(U-EDDA)(L)]$^-$ (L = CO_3^{2-}, ox, mal) using Bio-Rad AG 1-X8, 100–200 mesh, was not successful even though both isomers were known to be present for L = ox and mal. Substitution of Bio-Rad AG 2-X8, 100–200 mesh, for 1-X8 was similarly unsuccessful. Various column heights, eluent concentrations, drip rates, and resin ion types were used without success. It should be noted that [Co(U-EDDA)(CO_3)]$^-$, [Co(U-EDDA)(ox)]$^-$, and [Co(U-EDDA)(mal)]$^-$ are easily separated from one another on these resins because of different R_f values between complexes. Separation of cis and trans isomers within a species was accomplished by using fractional crystallization. We are currently investigating the separation of these and other analogous complexes on various carbohydrate type resins.

Characterization of the Isomers by Their ^1H NMR Spectra. It has been clearly demonstrated that the ^1H NMR resonance patterns of the methylene protons on the glycinate rings of EDDA, U-EDDA, and other similar ligands are critical in the assignment of the geometrical structure of various cobalt(III) compounds.[3,4,6,10] In all trans type compounds a single AB quartet is observed for the methylene protons in the range δ 3.1–4.8 (relative to NaDSS). In all but one cis type compound, an AB quartet and a singlet (collapsed AB quartet) corresponding to the methylene protons on the first and second glycinate rings are observed. Again the chemical shifts range from approximately δ 3.1 to 4.8. The lone exception is *cis*-[Co(U-EDDA)(en)]$^+$, where two overlapping quartets are observed.[6] In the trans cases the quartet integrates to four protons whereas in the cis compounds the quartet and singlet each integrate to two protons. Our present system exhibits these same patterns. With U-EDDA as ligand, however, the in-plane (relative to the ethylenediamine backbone) acetate arm is labeled G_2 and the out-of-plane arm R_2 (as compared to G_1 and R_1). The 2 indicates that the arm is attached to a tertiary amine. Tables I and II summarize the NMR spectra of all complexes reported in this study.

(1) The Trans U-EDDA Isomers. Both *trans*-[Co(U-EDDA)(tn)]$^+$ and *trans*-[Co(U-EDDA)(mal)]$^-$ exhibit a single AB quartet corresponding to the methylene protons on the two R_2 glycinate rings. For *trans*-[Co(U-EDDA)(tn)]$^+$ the en backbone and tn methylene resonances occur in the range δ 3.6–2.0. The theoretical ratio of en and tn methylene protons to the glycinate methylene protons is 2.50:1. Integration of our spectrum gives an experimental value of 2.55:1. (See Table I.) A fresh sample of *trans*-[Co(U-EDDA)(mal)]$^-$ (before the addition of concentrated H_2SO_4) shows a strong, but rapidly decreasing, singlet at δ 3.5. This peak is assigned to the methylene protons of the malonate ligand. Relatively rapid malonate proton exchange with D_2O has been previously reported.[3,11] Integration of the trans-[Co(U-EDDA)(mal)]$^-$ spectrum was not attempted until after the addition of concentrated H_2SO_4 and complete exchange of the malonate protons. Since there are four en methylene protons and four glycinate protons, a 1:1 integration ratio would be expected. Experimentally we obtained 1:1.06. For each complex J_{AB} = 17 Hz, comparing well with previously reported systems.[3,4,10]

---

(10) Blackmer, G. L.; Hamm, R. E.; Legg, J. I. *J. Am. Chem. Soc.* **1969**, *91*, 6632.

(11) Yoneda, H.; Morimoto, Y. *Inorg. Chim. Acta* **1967**, *1*, 413.

Table III. Electronic Absorption Spectral Data of the Reported Co(III)-(U-EDDA) Complexes

complex	λ_{max}, nm	ϵ, cm^{-1} M^{-1}
trans-[Co(U-EDDA)(tn)]$^+$	537	153
	465 (sh)	
	360	195
cis-[Co(U-EDDA)(tn)]$^+$	503	166
	361	191
trans-[Co(U-EDDA)(mal)]$^-$	569	178
	382	175
cis-[Co(U-EDDA)(mal)]$^-$	531	161
	381	141
cis-[Co(U-EDDA)(CO_3)]$^-$	535	169
	379	119
cis-[Co(U-EDDA)(ox)]$^-$	527	160
	375	143

The chemical shifts for H_A and H_B (A more downfield than B) are listed in Table II for each complex.

(2) The Cis U-EDDA Isomers. On the basis of previously established resonance patterns for EDDA uns-cis isomers[3,4] and the Co(III)-ED3A complex[10] (ED3A = ethylenediaminetriacetate), the cis U-EDDA isomers were easily identified. The cis isomers have a characteristic single AB quartet and an AB quartet that has collapsed to a singlet corresponding to the methylene protons of the G_2 and R_2 rings, respectively. In a fresh solution of *cis*-[Co(U-EDDA)(mal)]$^-$ an AB quartet also appears for the malonate protons, but these peaks decrease rapidly with time owing to deuterium exchange. In addition, resonance patterns corresponding to the en backbone protons (E ring) and tn methylene protons are observed at higher fields (δ 3.6-1.9). All cis U-EDDA spectra agree with the corresponding or analogous EDDA complexes except that in [Co(EDDA)(CO_3)]$^-$ the resonance for the G_1 ring has not totally collapsed to a singlet.[4] A doublet is observed at δ 3.52 and 3.49. In *cis*-[Co(U-EDDA)(CO_3)]$^-$ only a singlet is observed. Tables I and II summarize all the NMR data for the complexes studied.

Assignment of resonances in the cis complexes as being due to R_2 or G_2 rings is based upon C-N magnetic anisotropy effects. Using molecular models of our complexes and the arguments of Blackmer, Hamm, and Legg[10] concerning the [Co(ED3A)NO_2]$^-$ complex, we assign the singlet (collapsed AB quartet) to the methylene protons of the R_2 ring and the AB quartet resonances to the protons of the G_2 ring. Where quartets are observed, the low-field proton is designated A in each case.

Electronic Absorption Spectra. Visible absorption data served to provide supporting evidence in the structural assignment of the geometrical isomers. On the basis of the arguments and results presented by Legg and Cooke[12] and Chu, Cooke, and Liu[6] the molar absorptivities for the trans U-EDDA isomers would be expected to be greater than those for the corresponding cis isomers. This behavior was observed with [Co(U-EDDA)(mal)]$^-$. For the trans isomer, $\epsilon_{569} = 178$ and $\epsilon_{382} = 175$, whereas the cis isomer gives $\epsilon_{531} = 161$ and $\epsilon_{381} = 141$. (All λ in nm and ϵ in cm^{-1} M^{-1}.) The [Co(U-EDDA)(tn)]$^+$ isomers are not nearly as clear-cut, however. For *trans*-[Co(U-EDDA)(tn)]$^+$ $\epsilon_{537} = 153$ and $\epsilon_{360} = 195$, whereas for *cis*-[Co(U-EDDA)(tn)]$^+$ $\epsilon_{503} = 166$ and $\epsilon_{361} = 191$. *trans*-[Co(U-EDDA)(tn)]$^+$ exhibits the expected shoulder on the high-energy side of the low-energy peak.[6] Table III lists the pertinent visible spectral data for the complexes studied.

Acknowledgment. The authors express their appreciation to Dr. Joseph R. Crook of Western Washington University for his help in obtaining NMR spectra.

Registry No. *cis*-K[Co(U-EDDA)(CO_3)], 91670-31-4; Na_3[Co(CO_3)$_3$], 75632-02-9; *cis*-K[Co(U-EDDA)(mal)], 91670-32-5; *trans*-K[Co(U-EDDA)(mal)], 91739-91-2; *cis*-K[Co(U-EDDA)(ox)], 91670-33-6; *cis*-[Co(U-EDDA)(tn)]Cl, 91739-92-3; *trans*-[Co(U-EDDA)(tn)]Cl, 91670-34-7.

---

[12] Legg, J. I.; Cooke, D. W. *Inorg. Chem.* **1966**, *5*, 594.

Contribution from the Department of Chemistry,
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Solvatochromism of the LMCT Transition of Pentacyanoferrate(III) Complexes

Rex E. Shepherd,* M. Fazlul Hoq, Nancy Hoblack,
and Craig R. Johnson

Received October 6, 1983

The pentacyanoferrate(III) and pentaamineruthenium(III) complexes of imidazoles, pyrazoles, and pyridines substituted with functional groups having lone pairs in conjugation with the aromatic ring exhibit ligand-to-metal charge-transfer (LMCT) transitions in the visible region of the absorption spectrum.[1-6] Meyer et al. have shown that the solvatochromism of the pentaammineruthenium(III) complexes arises with specific interaction of hydrogen-bonding acceptor solvents with the coordinated NH_3 ligands.[4] As a consequence, the order of the positions of LMCT for the Ru(III) complexes or the MLCT transitions of the Ru(II) analogues were found to follow a solvent-dependent order related to Gutmann's donor number (DN).[4] The energies of the transitions increase with DN for the pentaammineruthenium(III) series and decrease for pentaammineruthenium(II), as anticipated for an increasingly anionic ligand field due to greater solvent-NH_3 hydrogen bonding. We wish to report here on the solvatochromism of pentacyanoferrate(III) complexes.

Results and Discussion

Unlike the pentaammineruthenium(III) series, we have found that the solvatochromic behavior of pentacyanoferrate(III) complexes is well-correlated with the Reichardt-Dimroth (E_T)[7] and Kosower (Z)[8] scales. The E_T and Z scales of solvents are based on the shift in the charge-transfer transitions of pyridinium *N*-phenolbetaine and ethyl-4-(carbomethoxy)pyridinium iodide dye molecules.[7,8] The solvent scales relate the ability of a dissolved dipole to polarize the solvent.[9] The behavior of the LMCT band of $(CN)_5FeL^{2-}$

---

[1] Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2754-2763.

[2] Shepherd, R. E. *J. Am. Chem. Soc.* **1976**, *98*, 3329-3335.

[3] Sundberg, R. J.; Bryan, R. F.; Taylor, I. F.; Taube, H. *J. Am. Chem. Soc.* **1974**, *96*, 381-392.

[4] Curtis, J. C.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 224-236.

[5] Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 3506-3513.

[6] Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 4021-4023.

[7] Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29-40 and references therein.

[8] (a) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253-3270. (b) Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368-3375. (c) See also 10 other references to Kosower's papers in ref 7.

[9] (a) Brooker, L. G. S.; Keyes, G. H.; Sprague, R. H.; Van Dyne, R. H.; VanLare, E.; VanZandt, G.; White, F. L. *J. Am. Chem. Soc.* **1951**, *73*, 5326-5336. (b) Reference 7, p 34. (c) Johnson, C. R.; Shepherd, R. E. *Synth. React. Inorg. Met-Org. Chem.* **1984**, *14*, 339-353.

[10] Purification procedures and solvent properties may be obtained through the following references and their bibliographies: (a) Coetzee, J. F.; Istone, W. K. *Anal. Chem.* **1980**, *52*, 53-59. (b) Coetzee, J. F.; Frollini, D.; Karakatsanis, C. G.; Subak, E. J.; Umemoto, K. In "Characterization of Solutes in Nonaqueous Solvents"; Mamantov, G., Ed.; Plenum Press: New York, 1978; p 1.

0020-1669/84/1323-3249$01.50/0