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Iminodiacetato, Methyliminodiacetato, and 1,3-Propanediaminetetraacetato Complexes of Chromium(III)

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Several complexes of chromium(III) with iminodiacetic acid (H_2IDA), methyliminodiacetic acid (H_2MIDA), and 1,3-propanediaminetetraacetic acid (H_4(1,3-PDTA)) have been prepared and characterized. Bis complexes with the *cis* configuration (with respect to the nitrogens) have been prepared in the case of IDA [$HN(CH_2COO^-)_2$], and the mixed complex containing IDA and MIDA [$CH_3N(CH_2COO^-)_2$]. No *trans* isomer was found in either case. The bis complex containing MIDA formed only the facial *trans* isomer. Both IDA and MIDA form mono complexes which have been prepared and isolated in solution. The complex formed with 1,3-PDTA [$(^-OOCCH_2)_2NCH_2CH_2CH_2N(CH_2COO^-)_2$] is also reported. The complexes were prepared and characterized using ion-exchange chromatography and visible and infrared absorption spectra.

Complexes of cobalt(III) with iminodiacetic acid,[1-3] methyliminodiacetic acid,[3] and 1,3-propanediaminetetraacetic acid[4] have recently been prepared and extensively characterized. Very recently, the H_2IDA and H_2MIDA complexes of rhodium(III) have been reported.[5] Such has not been the case with chromium(III). Recently, a red complex $K[Cr(IDA)_2]$ was reported,[6] but no speculation was made as to which geometrical isomer was obtained or whether more than one geometrical isomer was present in the reaction mixture. Also, an orange complex $NH_4[Cr(MIDA)_2]$ has recently been reported[7,8] but again no speculation was made as to which geometrical isomer was obtained. At the time this study was begun, no chromium(III) complexes with IDA or MIDA as ligands had been reported.

There are three possible geometrical isomers for the bis complexes, and these are shown in Figure 1. Previous work[9] has indicated that IDA and MIDA strongly prefer the facial configuration, and only one complex each has been reported where IDA and MIDA are occupying the meridional configuration.

Our purpose was to prepare this series of complexes, both the bis and the mono species, and assign either the *cis* or *trans* (facial or meridional) configuration to the bis complexes. During the course of the investigation we also prepared the chromium(III)–1,3-PDTA complex.

Experimental Section

Chemicals.—All chemicals used were reagent grade or chemically pure. The water used was deionized and boiled to remove all CO_2.

Spectral Measurements.—All visible absorption spectral measurements were made on a Cary Model 14 recording spectrophotometer or a Beckman Model DB spectrophotometer attached to a Sargent Model SRL recorder. All molar absorptivity values were obtained on the Cary 14 using water as solvent. The spectra were recorded at 25 and 29°, the molar absorptivities of the six complexes being unaffected, within experimental error, over this temperature range. Beer's law was checked and was found to be obeyed by all six species.

All ir spectra were taken on the Beckman IR-8 spectrophotometer using potassium bromide pellets.

Potassium *cis*-Bis(iminodiacetato)chromate(III).—This complex was prepared by a method similar to that outlined by Yamasaki and Ito.[6] To 125 ml of an aqueous solution containing 19.8 g (0.30 mol) of 85% KOH was added 20.0 g (0.15 mol) of H_2IDA. To this solution was added 20.0 g (0.075 mol) of chromium(III) chloride hexahydrate. The reaction mixture was heated on a steam bath for 2 hr (volume approximately 75 ml). After cooling, red crystals were obtained and filtered. The crude product was recrystallized from warm water, washed with ethanol–water mixtures and finally 100% ethanol, and air dried. The yield was 20 g, approximately 67%. The solid contains 2.50 waters of crystallization which are lost at 120°. *Anal.* Calcd for *cis*-$K[Cr(IDA)_2]\cdot 2.5H_2O$: Cr, 13.06; C, 24.12; H, 3.80; N, 7.03; H_2O, 11.31. Found: Cr, 13.02; C, 23.95; H, 3.79; N, 7.01; H_2O, 11.47.

Iminodiacetatotriaquochromium(III) Cation.—To 100 ml of H_2O containing 2.66 g (0.01 mol) of chromium(III) chloride hexahydrate was added 1.33 g (0.01 mol) of H_2IDA. The solution was heated to 70° for 1 hr and then cooled. To this solution was added 1.32 g (0.02 mol) of 85% KOH and heating was continued for 3 hr. After cooling, the solution was filtered and was then introduced into a 2.5 cm × 40 cm column containing Dowex 50W-X8 (100–200 mesh) cation-exchange resin in the Na^+ form. The column was maintained at room temperature. This captured all positively charged species, allowing a separation from any zero or negatively charged species. After washing the column with H_2O, elution of the $Cr(IDA)(H_2O)_3^+$ cation was begun using 0.1 *M* NaCl as eluent. A single band with +1 charge characteristics was observed during elution with a band containing hexaaquochromium(III) ion remaining unmoved at the top of the column. Elution gave a solution about 10 m*M* in the desired complex. Preparation of this cation following the same procedure except using $Cr(NO_3)_3\cdot 9H_2O$ in place of $CrCl_3\cdot 6H_2O$ and eluting with $NaNO_3$ gave identical results. The complex was analyzed in solution for chromium and nitrogen. Results: Cr:N = 1.007:1.000.

Sodium *trans*-Bis(methyliminodiacetato)chromate(III).—To 125 ml of an aqueous solution containing 12.0 g (0.30 mol) of NaOH was added 22.1 g (0.15 mol) of H_2MIDA. Then 20.0 g (0.075 mol) of chromium(III) chloride hexahydrate was added and the solution was heated on a steam bath for 2 hr. After cooling, orange crystals were obtained and collected. This material was recrystallized from warm H_2O, washed with ethanol–water mixtures, and air dried. The yield was 18 g, approximately 66%. The potassium, ammonium, and hydrogen forms of this

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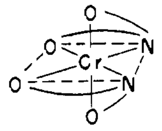

CIS

TRANS (FACIAL)

TRANS (MERIDIONAL)

Figure 1.—The three possible geometrical isomers of the bis complexes.

complex were also prepared, but their solubility is much less than the sodium salt; hence the sodium salt was chosen. The sodium salt contains no water of crystallization. *Anal.* Calcd for *trans*-Na[Cr(MIDA)$_2$]: Cr, 14.24; C, 32.89; H, 3.86; N, 7.67. Found: Cr, 14.29; C, 33.01; H, 3.91; N, 7.72.

Methyliminodiacetatotriaquochromium(III) Cation.—This species was prepared in a manner analogous to the Cr(IDA)(H$_2$O)$_3^+$ species, except using H$_2$MIDA in place of H$_2$IDA. The column behavior and characteristics of the Cr(MIDA)(H$_2$O)$_3^+$ species are very similar to the analogous IDA compound. The properties of the mono-MIDA species were independent of the method of preparation. The compounds CrCl$_3$·6H$_2$O and NaCl or Cr(NO$_3$)$_3$·9H$_2$O and NaNO$_3$ gave identical products. The species was analyzed in solution for chromium and nitrogen. Results: Cr:N = 0.996:1.000.

Ammonium *cis* Iminodiacetatomethyliminodiacetatochromate(III).—To 40 g (0.10 mol) of Cr(NO$_3$)$_3$·9H$_2$O in 30 ml of H$_2$O was added 30 ml of concentrated NH$_4$OH. This mixture was then centrifuged and the solution was decanted. A small amount of water was added, and the mixture was again centrifuged and decanted. The chromium hydroxide was transferred to a beaker containing 200 ml of H$_2$O. To this mixture was added 13.3 g (0.10 mol) of H$_2$IDA and 6 ml of concentrated HNO$_3$. This solution was heated at 70° for 3-4 hr, cooled, and filtered. Then 14.7 g (0.10 mol) of H$_2$MIDA and 13.2 g (0.20 mol) of 85% KOH was added. This solution was allowed to stand at room temperature for 4 days and was then filtered.

The solution was then introduced into a 7 cm × 60 cm column containing Dowex 1-X8 (100–200 mesh) anion-exchange resin in the Cl$^-$ form. The column was maintained at room temperature. After charging was complete, the column was washed with H$_2$O. Elution was carried out with 0.15 *M* KCl. Three separate bands containing −1 charged species were obtained on the column. No other higher charged species were present. The three bands were identified as the following: (1) *trans*-Cr(MIDA)$_2^-$ (identified by visible and infrared spectra) which eluted very much faster than the other two bands (no N–H stretching frequency was found in this complex, indicating the absence of IDA), (2) *cis*-Cr(IDA)(MIDA)$^-$, and (3) *cis*-Cr(IDA)$_2^-$. Bands 2 and 3 had very similar elution characteristics, but good separation was achieved on careful development of the column. Band 3 was identified as *cis*-Cr(IDA)$_2^-$ using its visible absorption spectrum.

The solution containing the desired pure complex was evaporated to a concentration of approximately 0.08 *M*, and then an equivalent amount of BaCl$_2$ was added to the solution. A volume of ethanol was added, approximately 70% of the volume of water present, and the precipitate was filtered and washed with ethanol–water mixtures and finally 100% ethanol. This salt appears to have the rough stoichiometry BaCl[Cr(IDA)(MIDA)]; however, the salt also contains some potassium ion in place of barium ion and has a powdery, noncrystalline form. The crude barium salt, 10 g, was dissolved in 70 ml of H$_2$O and passed through a column containing 60 ml of Dowex 50W-X8 (50–100 mesh, 1.92 mequiv/ml wet volume) cation-exchange resin in the NH$_4^+$ form. To the resulting solution (80 ml) was added, in 80-ml increments, 480 ml of 100% ethanol. The resulting clear solution was cooled to 0°, and a pink crystalline product was deposited. The crystals were filtered, washed with a 7:1 ethanol–water mixture and finally 100% ethanol, and air dried. Both the ammonium and the potassium salts of this complex are more soluble than the *cis*-K[Cr(IDA)$_2$] complex, and the potassium salt is somewhat hygroscopic. The ammonium salt, however, is not hygroscopic. The ammonium salt contains one water of crystallization which is lost at 100°. Five grams of the ammonium salt was obtained, approximately 14% yield. *Anal.* Calcd for *cis*-NH$_4$[Cr(IDA)(MIDA)]·H$_2$O: Cr, 14.28; C, 29.68; H, 4.98; N, 11.54; H$_2$O, 4.95. Found: Cr, 14.33; C, 29.74; H, 5.04; N, 11.37; H$_2$O, 4.37.

1,3-Propanediaminetetraacetic Acid.—Schwarzenbach and Ackermann[10] reported that H$_4$(1,3-PDTA) did not precipitate upon the acidification of the condensation mixture of monochloroacetic acid, sodium hydroxide, and 1,3-propanediamine. Tanaka and Ogino[4] were able to precipitate the acid from the condensation mixture by careful adjustment of the pH. We have devised another method for obtaining the acid from the condensation mixture which gives very good yields.

Monochloroacetic acid (86 g, 0.91 mol) was dissolved in 75 ml of H$_2$O and cooled in an ice bath. Then 58 g (0.88 mol) of 85% KOH, dissolved in 90 ml of H$_2$O and cooled in an ice bath, was added drop by drop to the solution with stirring. The temperature of the solution did not rise above 20°. 1,3-Propanediamine (15 g, 0.20 mol) was added and the solution was heated on the steam bath for 2 hr. Immediately after placing the solution on the steam bath, 58 g (0.88 mol) of 85% KOH in about 60 ml of H$_2$O was added in such a manner so that the pH remained at about 8. The solution was evaporated to about 200 ml and cooled to 0°, and the deposited KCl was removed by filtration. Then 98 g (0.40 mol) of BaCl$_2$·2H$_2$O was dissolved in 180 ml of H$_2$O at 90°, and this solution, while still hot, was added to the reaction mixture. The mixture was stoppered and shaken vigorously for 0.5 hr. During this period, white Ba$_2$(1,3-PDTA) precipitated out of solution. This precipitate was filtered, washed with warm water, and dried under vacuum at 95°. An equivalent amount of 2 *N* H$_2$SO$_4$ was added to a slurry of the solid, and the BaSO$_4$ was removed by filtration. The volume of the clear filtrate was evaporated on a steam bath to 150 ml and cooled. Then ethanol was added, and the mixture was triturated until white crystals of the acid were obtained. The crude product was recrystallized from an ethanol–water mixture and dried at 105°. The yield was 37 g, approximately 60%. *Anal.* Calcd for C$_{11}$H$_{18}$N$_2$O$_8$: C, 43.14; H, 5.92; N, 9.15. Found: C, 43.06; H, 5.95; N, 9.09.

Sodium 1,3-Propanediaminetetraacetatochromate(III).—To 200 ml of a solution containing 4.0 g (0.10 mol) of NaOH was added 15.5 g (0.05 mol) of H$_4$(1,3-PTDA). The solution was heated to 70° and 20.0 g (0.05 mol) of Cr(NO$_3$)$_3$·9H$_2$O was added. After heating for a period, 4.0 g of NaOH was again added and heating was continued at 70° for 12 hr, with evaporation reducing the volume to 125 ml. The solution was cooled to 0° in an ice bath, and the deposited red crystals were filtered and collected. The product was recrystallized by dissolving in a small amount of H$_2$O, warming, adding an equal volume of ethanol, and then cooling. The crystals were filtered, washed with ethanol–water mixtures and finally pure ethanol, and air dried. The salt contains three waters of crystallization which are

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[10] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

lost by heating at 120°. The yield was 13 g, approximately 60%. *Anal.* Calcd for $Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$: Cr, 12.06; C, 30.64; H, 4.67; N, 6.50; H_2O, 12.53. Found: Cr, 12.14; C, 30.74; H, 4.70; N, 6.46; H_2O, 12.45.

Methods of Analysis.—The chromium analyses were performed by dissolving the sample in 2 *N* H_2SO_4, adding excess ammonium peroxydisulfate, and adding a small amount of silver nitrate solution as a catalyst. The solution was boiled for 45 min to destroy the excess peroxydisulfate, and, to the dichromate formed, a measured excess of standard ferrous solution was added. The excess ferrous ion was back-titrated with standard dichromate using diphenylaminesulfonate ion as indicator.

Nitrogen, for the two cationic species which were prepared in solution, was determined by the Kjeldahl method.

The water of crystallization in the various complexes was determined by weight loss after heating to a constant weight.

The carbon, hydrogen, and nitrogen analyses on the solid samples were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Various reaction mixtures containing iminodiacetate ion and chromium(III) ion from chromium(III) nitrate, chromium(III) chloride, or chromium(II) ion were prepared under various pH, temperature, and time conditions. These solutions were chromatographed on a column containing Dowex 1-X8 anion-exchange resin in either the chloride or the nitrate form, and in all cases, upon elution of the column with 0.1 *M* KCl or KNO_3, only one band (red) was observed. Since three geometrical isomers are possible for the bis(iminodiacetato)chromate(III) complex, assignment must be made as to which geometrical isomer had been obtained.

It would appear that the *trans* meridional isomer would be the least likely of the three to be formed in abundance, since the work of Legg and Cooke[9] suggests that IDA prefers the facial configuration to the meridional configuration. They report a small yield of *trans* (meridional)-iminodiacetato(diethylenetriamine)cobalt(III) ion, the first reported complex of IDA in a meridional configuration.

It should be possible to assign either the *cis* or one of the *trans* configurations to the bis-IDA complex by comparing its visible spectrum and ion-exchange elution behavior with other known *cis* and *trans* compounds containing two nitrogen and four oxygen atoms coordinated to chromium(III).

Known *cis* compounds are the bis(oxalato)ethylenediaminechromate(III) ion ($Cr(en)(C_2O_4)_2^-$, where en is ethylenediamine),[11] tetraaquoethylenediaminechromium(III) cation ($Cr(en)(H_2O)_4^{3+}$),[12] and the ethylenediaminetetraacetatochromate(III) ion ($Cr(EDTA)(H_2O)^-$, where EDTA is the ethylenediaminetetraacetate anion).[13] The $Cr(EDTA)(H_2O)^-$ species should probably not be used for comparison, however, because of its dissimilarity in symmetry to the complexes under consideration. A better choice for comparison would be the chromium(III) complex with 1,3-propanediaminetetraacetate ion, since less strain should be present in the ligand backbone and allow coordination of all four acetate groups. This compound has not been previously reported in the literature, and hence we report its characterization here.

Known, characterized *trans*-chromium(III) complexes of this type are very rare, but according to Cooke,[3] in the analogous Co–MIDA system, only *trans*-(facial)-$Co(MIDA)_2^-$ is formed. No *cis*-$Co(MIDA)_2^-$ is formed because of steric interactions between the methyl groups. Similar results are obtained in the rhodium(III) case.[5] The preparation of the bis-MIDA complex of chromium(III) would be expected to yield preferentially, then, the *trans* isomer.

Various reaction mixtures containing methyliminodiacetate ion and chromium(III) ion were prepared under various conditions and the solutions were chromatographed on an ion-exchange column containing Dowex 1-X8 anion-exchange resin. Here again only one band was observed on elution with 0.1 *M* NaCl or $NaNO_3$. The band was orange, and orange crystals could easily be obtained upon partial evaporation of the solution obtained from the column.

It would also be of interest to prepare the mixed IDA–MIDA complex of chromium(III) and determine which isomers are formed. Ion-exchange chromatography showed that only one geometrical isomer was formed.

The visible absorption spectra and molar absorptivities of the $Cr(IDA)_2^-$, $Cr(IDA)(MIDA)^-$, $Cr(MIDA)_2^-$, $Cr(1,3\text{-}PDTA)^-$, $Cr(en)(C_2O_4)_2^-$, and $Cr(en)(H_2O)_4^{3+}$ ions are shown in Table I. The visible absorption spectral curves for $Cr(IDA)_2^-$, $Cr(MIDA)_2^-$, and $Cr(1,3\text{-}PDTA)^-$ are given in Figure 2. It is to be noted that the peak positions of the $Cr(IDA)_2^-$ and $Cr(IDA)(MIDA)^-$ species are very similar to the $Cr(1,3\text{-}PDTA)^-$, $Cr(en)(C_2O_4)_2^-$, and $Cr(en)(H_2O)_4^{3+}$ species, all *cis* compounds. More specifically, the low-energy peak in each case, 519 and 518 mμ for $Cr(IDA)_2^-$ and $Cr(IDA)(MIDA)^-$, respectively, falls in the middle of the range of the other three known *cis* complexes. Both peaks of the $Cr(MIDA)_2^-$ species are shifted 15–20 mμ to higher energy, as compared with

TABLE I

VISIBLE ABSORPTION SPECTRA OF THE VARIOUS CHROMIUM(III) COMPLEXES

$Na[Cr(MIDA)_2]$[a]	362[b] (29[c]), 403 (13, min), 495 (42)
$K[Cr(IDA)_2]\cdot 2.5H_2O$[a]	391 (79), 442 (26, min), 519 (76)
$NH_4[Cr(IDA)(MIDA)]\cdot H_2O$[a]	393 (53), 442 (24, min), 518 (55)
$Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$[d]	385 (83), 433 (30, min), 509 (118)
$K[Cr(en)(C_2O_4)_2]\cdot 2H_2O$[e]	395 (94.4), 452 (19.4 min), 530 (88.0)
$Cr(en)(H_2O)_4^{3+}$ [f]	385 (24.3), 433 (10.7, min), 512 (41.7)
$Cr(EDTA)(H_2O)^-$ [g]	395 (106), 545 (202)
$Cr(IDA)(H_2O)_3^+$ [h]	393 (50), 460 (13, min), 544 (60)
$Cr(MIDA)(H_2O)_3^+$ [i]	393 (48), 462 (11, min), 553 (60)

[a] Concentration 0.010 *M*. [b] Wavelength given in millimicrons (mμ). [c] Units are M^{-1} cm^{-1}. [d] Concentration 0.0050 *M*. [e] Reference 11. [f] Reference 12. [g] Reference 13 and G. den Boef and B. C. Poeder, *Anal. Chim. Acta*, **30**, 261 (1964). [h] Concentration 0.00771 *M* in 0.04 *M* HCl and 0.21 *M* KCl. [i] Concentration 0.00907 *M* in 0.04 *M* HCl and 0.21 *M* KCl.

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(11) H. L. Schläfer, O. Kling, L. Mahler, and H. P. Opitz, *Z. Physik. Chem.*, **24**, 307 (1960).

(12) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749 (1968).

(13) R. E. Hamm, *J. Am. Chem. Soc.*, **75**, 5670 (1953).

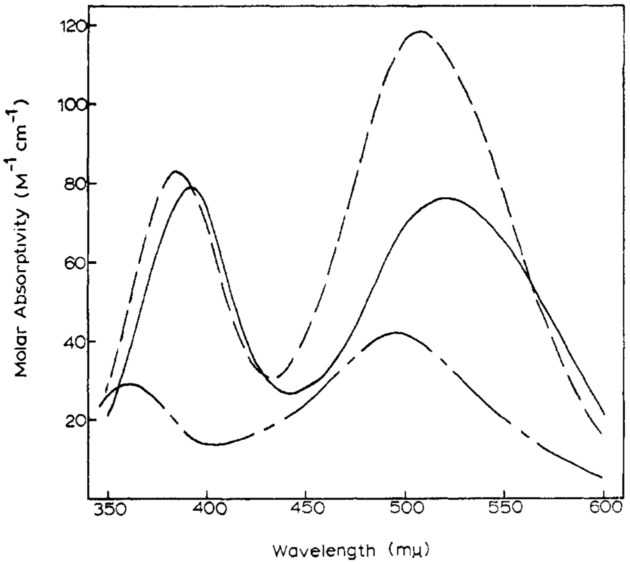

Figure 2.—The visible absorption spectrum of the $Cr(IDA)_2^-$ ion (———), the $Cr(MIDA)_2^-$ ion (— - —), and the Cr(1,3-PDTA)$^-$ ion (— — —).

the highest energy absorbing *cis* complex. The similarity of the peak positions of the $Cr(IDA)_2^-$ and Cr(IDA)(MIDA)$^-$ species to the other *cis* complexes would support the assignment of the *cis* configuration to these two complexes. Because of the relatively large difference in the position of the absorption peaks of the $Cr(MIDA)_2^-$ species, this complex could be assigned the *trans* configuration, as expected, since the presence of the methyl groups instead of hydrogen on the nitrogens would not be expected to change the positions of the absorption peaks significantly if the geometric configurations were the same. One also notes the relatively large values for the molar absorptivities for the $Cr(IDA)_2^-$, Cr(IDA)(MIDA)$^-$, Cr(1,3-PDTA)$^-$, and $Cr(en)(C_2O_4)_2^-$ species in comparison with the $Cr(MIDA)_2^-$ ion. These relative values again support the assignment of the *cis* configuration to the $Cr(IDA)_2^-$ and Cr(IDA)(MIDA)$^-$ ions and the *trans* configuration to $Cr(MIDA)_2^-$, since the low molar absorptivities indicate a high degree of symmetry for the $Cr(MIDA)_2^-$ ion, in agreement with the *trans* configuration. The molar absorptivities of the $Cr(en)(H_2O)_4^{3+}$ ion are not compared because of the presence of only a single chelate ring. The very low molar absorptivities for the $Cr(MIDA)_2^-$ ion also support the assignment of the configuration as being the *trans* facial isomer. In the only case[9] where MIDA has been found to be occupying the meridional position, *i.e.*, the *trans*-Co(dien)(MIDA)$^+$ ion, where dien is diethylenetriamine, the molar absorptivities were very high in comparison with the *cis* isomer of the same complex, where MIDA is occupying the facial position. This was attributed to the strain involved when MIDA is occupying the meridional position, causing the loss of a center of symmetry.

Next, the elution properties of the $Cr(MIDA)_2^-$, $Cr(IDA)_2^-$, Cr(IDA)(MIDA)$^-$, Cr(1,3-PDTA)$^-$, and $Cr(en)(C_2O_4)_2^-$ species were compared on a 2.5 cm × 40 cm column containing Dowex 1-X8 anion-exchange resin (100–200 mesh) in the chloride form. Elution was performed at room temperature using 0.1 *M* NaCl and the elution rate was approximately 3 drops/min. The *trans* isomer, having a relatively smaller polar character, should be eluted before the *cis* isomers.[14] Also, the *cis* isomers should have approximately similar elution characteristics, because of their similarity of configuration. Amounts of 0.25-mmol of each complex[15] were mixed together and added to 10 ml of H_2O, and this solution was used to charge the column. From the separations achieved on this column, the following relative R_f values can be assigned: $Cr(IDA)_2^-$, 1.0; Cr(1,3-PDTA)$^-$, 1.3; Cr(IDA)(MIDA)$^-$, 1.5; $Cr(en)(C_2O_4)_2^-$, 2.0; $Cr(MIDA)_2^-$, 3.2. Complete separation of the Cr(1,3-PDTA)$^-$ and Cr(IDA)(MIDA)$^-$ bands was not achieved, and the column actually contained four well-defined bands. The fact that the $Cr(MIDA)_2^-$ species was eluted very much faster than the other species is again good evidence for the assignment of the *trans* configuration to this complex. Since the $Cr(IDA)_2^-$ species was eluted after and the Cr(IDA)(MIDA)$^-$ species was almost indistinguishable from the *cis* compound Cr(1,3-PDTA)$^-$, this again points to the *cis* configuration for these two compounds.

The infrared spectra of $K[Cr(IDA)_2]\cdot 2.5H_2O$, $Na[Cr(MIDA)_2]$, $NH_4[Cr(IDA)(MIDA)]\cdot H_2O$, and $Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$ were taken using KBr pellets. The ir spectrum of the crude BaCl[Cr(IDA)(MIDA)] salt was also taken to note the presence of the N–H stretch, thus confirming the presence of IDA in the mixed complex. The results of these spectra are given in Table II. The sharpness and position of the carboxyl stretching frequency tends to support the equivalence and coordination of all four carboxyl groups in the four complexes. The ir spectra of these same complexes taken in a Nujol slurry indicated that no decomposition occurred in preparation of the KBr pellet.

TABLE II

INFRARED ASYMMETRICAL CARBOXYLATE AND N–H STRETCHING FREQUENCIES FOR THE COMPLEXES[a,b]

Complex	COOM	N–H
trans(facial)-$Na[Cr(MIDA)_2]$	1638 s	
cis-$K[Cr(IDA)_2]\cdot 2.5H_2O$	1640 s	3225 m
$Na[Cr(1,3\text{-}PDTA)]\cdot 3H_2O$	1638 s 1670 sh	
cis-$NH_4[Cr(IDA)(MIDA)]\cdot H_2O$	1635 s	3180 m, br
cis-BaCl[Cr(IDA)(MIDA)]	1635 s	3080 m

[a] Frequencies are given in wave numbers, cm^{-1}. [b] Abbreviations: s, strong; m, medium; sh, shoulder; br, broad.

The relative solubilities of the potassium salts of the $Cr(IDA)_2^-$, Cr(IDA)(MIDA)$^-$, and $Cr(MIDA)_2^-$ ions also support the assignment of the *cis* configuration to the $Cr(IDA)_2^-$ and Cr(IDA)(MIDA)$^-$ ions and the *trans* configuration to the $Cr(MIDA)_2^-$ ion. The relative solubilities in water are in the order $K[Cr(MIDA)_2] << K[Cr(IDA)_2] < K[Cr(IDA)(MIDA)]$.

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(14) G. B. Kauffman, R. P. Pinnell, and L. T. T. Takahashi, *Inorg. Chem.*, **1**, 544 (1962), and references therein.

(15) The potassium salt of the $Cr(en)(C_2O_4)_2^-$ complex was supplied in pure form by T. W. Kallen of this laboratory.

The smaller solubility of the *trans* species is to be expected because of its smaller dipole moment in comparison with the *cis* complexes.

We believe, then, on the basis of the experimental evidence obtained, that the following assignments are justified for the IDA–MIDA series of bis complexes: *cis*-$K[Cr(IDA)_2]\cdot 2.5H_2O$; *cis*-$NH_4[Cr(IDA)(MIDA)]\cdot H_2O$; *trans*(facial)-$Na[Cr(MIDA)_2]$.

The distinctive differences between the $Cr(EDTA)(H_2O)^-$ complex and the $Cr(1,3\text{-}PDTA)^-$ complex should be noted. Adding one more methylene link to the backbone of the ligand has apparently relieved almost all strain and has allowed 1,3-PDTA to function apparently as a hexadentate ligand, very much different from the Cr(III)–EDTA complex where EDTA functions as a pentadentate ligand,[13] with a water molecule in the sixth coordination position and an acetate arm remaining free. Molecular models show that strain inherent in the ethylenediamine backbone hinders the ability of EDTA to function as a hexadentate ligand. The symmetry of the $Cr(EDTA)(H_2O)^-$ complex differs from the $Cr(1,3\text{-}PDTA)^-$ complex and this is exemplified in comparing the values of the molar absorptivities for the two complexes. These data are given in Table I. It is also noted that the low-energy absorption band of the EDTA complex has been shifted from the expected value of 510–530 mμ to 545 mμ.

It was also of interest to prepare and compare the visible absorption spectra and molar absorptivities of the mono-IDA and mono-MIDA complexes of chromium(III). Since these species would have a +1 charge, their separation from a reaction mixture containing hexaaquochromium(III) ion (+3 in charge) and the bis complex of the corresponding ligand (−1 in charge) could easily be effected using ion-exchange chromatography. The preparation of these mono species was not clean, some hexaaquochromium(III) ion and the bis complex always being present. The iminodiacetatotriaquochromium(III) ion and the methyliminodiacetatotriaquochromium(III) ion were, however, the major species formed in each case. Both mono species appear to be quite stable with respect to disproportionation into the hexaaquochromium(III) ion and the bis complex. After separation and purification of the mono species by ion exchange and allowing the solutions to sit at room temperature for 1 week, reintroduction of these solutions onto a cation-exchange column showed no or very little evidence for the presence of the hexaaquochromium(III) ion or the bis complex.

The visible absorption spectra and molar absorptivities of these two complexes are given in Table I. The molar absorptivities of the two ions are essentially identical at the two maxima. The only noticeable difference in the two spectra is the fact that in the mono-MIDA complex the low-energy peak has been slightly shifted to longer wavelengths in comparison with the mono-IDA complex.

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Cyclic Voltammetric Study of the Rate of Ligand Exchange between Cadmium Ion and Calcium Ethylenediaminetetraacetate[1a,b]

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The rate of ligand exchange between calcium ethylenediaminetetraacetate complex ion and cadmium ion is measured using the technique known as cyclic stationary electrode polarography. In the presence of excess calcium ion the reaction is found to proceed through (1) a pathway involving a fast, acid-catalyzed dissociation of the calcium complex followed by a rate-limiting combination of the free monoprotonated ligand with cadmium ion and (2) a pathway involving a direct attack of the complex by cadmium ion. At 25° the second-order rate constant for the first pathway is $2.6 \pm 0.7 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ and for the second pathway is $2.3 \pm 0.2 \times 10^2\ M^{-1}\ \text{sec}^{-1}$. The direct reaction is found to proceed through an intermediate in which the multidentate ligand is half-unwrapped and partially bound to both calcium and cadmium ions. The rate-limiting step in both pathways appears to be the formation of the initial cadmium–nitrogen bond.

Introduction

The kinetics and mechanisms of the electrophilic exchange of ethylenediaminetetraacetic acid (EDTA) anion between two metal ions have been studied for several different systems using a variety of techniques. Studies making use of dc polarography,[2-4] radioisotopic

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