latter calculations which correspond closely to the electron-deficient model, reproduce the experimental trends much better than the calculations with d functions. The actual bonding situation in these phosphoranes is intermediate between models 1 and 2. Ab initio calculations for PF_5 report populations of d functions between 0.64[39] and 1.13 au.[40] Furthermore, polar contributions to both axial and equatorial bonds have to be considered.

Acknowledgment. H.O. and B.S. gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft.

Registry No. $PClF_4$, 13637-88-2; PCl_2F_3, 13454-99-4; PCl_3F_2, 13537-23-0; PCl_4F, 13498-11-8.

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Solution Structure of [Cr^{III}(L)(O-O)]^n Complexes (L = Nitrilotriacetate, *N*,*N*-β-Alaninediacetate; O-O = Malonate, Oxalate, Acetylacetonate, 2H_2O) and Characterization of [Cr(nta)(OH)]$_2^{2-}$ by Deuteron NMR Spectroscopy

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Received July 31, 1985

The complexes [Cr^{III}(L)(O-O)]^n (L = nitrilotriacetate (nta), *N*,*N*-β-alaninediacetate (β-alada); O-O = malonate (mal), oxalate (ox), acetylacetonate (acac), 2H_2O) have been synthesized, chromatographically purified, and characterized by deuteron NMR, infrared and electronic absorption spectroscopy. The two possible isomers, symmetrical (sym) and unsymmetrical (unsym), for [Cr(β-alada)(acac)]$^-$ and [Cr(β-alada)(mal)]$^{2-}$ were isolated, but only the unsym isomer for [Cr(β-alada)(ox)]$^{2-}$ was found. The starting materials for the synthesis of these complexes, [Cr(nta)(OH)]$_2^{2-}$ and *unsym*-[Cr(β-alada)(H_2O)$_2$], were also characterized. Both species were shown to be in equilibrium with the corresponding monomer and dimer, respectively. The chemistry of the various species investigated differs, to some extent, from what has been previously reported. The recent availability of a readily applicable NMR technique for the study of Cr(III) chemistry (^{2}H NMR) has greatly facilitated these studies.

Introduction

Numerous studies of the aminetricarboxylate ligand (N(–O)$_3$) complexes of the substitution-inert metal ions chromium(III)[2-7] and cobalt(III)[2,8-10] have been reported. When these tripodlike ligands function as quadridentate chelating agents, two cis sites remain (Figure 1). Complexes such as these, where the two remaining sites are occupied by water molecules, exhibit a propensity to dimerize in aqueous solution to give bis(μ-hydroxo)-bridged species.[8,11-18] The Co(III) complex of the tripodlike ligand nitrilotriacetate (nta)[19] readily forms a bis(μ-hydroxy)-bridged dimer.[8] Absorption spectral studies of Cr(III) complexes of these two ligands as well as of another nta analogue, *N*,*N*-β-alaninediacetate (β-alada), have concluded that N(–O)$_3$ ligands can function both as quadridentate and terdentate (three acetates coordinated) chelating agents, but dimer formation was not reported.[2,5-7]

The studies of Co(III)–nta complexes were facilitated significantly by ^{1}H NMR spectroscopy.[20] Unfortunately, until recently it has not been possible to do structural studies on Cr(III) complexes by NMR due to the extreme line broadening of resonances brought about by the long electron spin relaxation times associated with paramagnetic Cr(III). Recently we have demonstrated that ^{2}H NMR can be used to study the solution chemistry of Cr(III) complexes.[21-23] Since N(–O)$_3$ ligands can be prepared readily

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(19) Abbreviations: nta = nitrilotriacetate; β-alada = *N*,*N*-β-alaninediacetate; acac = acetylacetone (1,3-pentanedione); mal = malonate; ox = oxalate; gly = glycinate.

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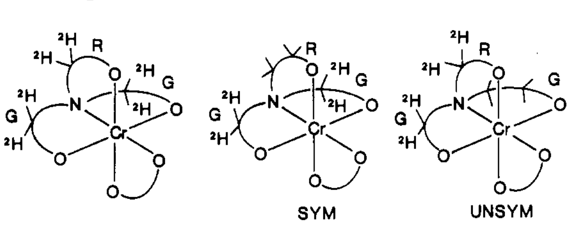

Figure 1. Possible structures for complexes with nitrilotriacetate-d_6 (nta-d_6) and *N,N*-β-alaninediacetate-d_4 (β-alada-d_4). SYM = symmetrical, UNSYM = unsymmetrical.

with deuterium substituted at the α-carbons of the acetates, we were able to investigate the solution behavior of Cr(III) complexes with nta and β-alada by ^{2}H NMR spectroscopy as described in this report. Complexes with two cis sites blocked with a bidentate ligand (mal, ox, acac), thereby inhibiting dimerization, were studied in order to define the mode of ligand coordination (e.g. quadri- or terdentate chelation). The results of these studies facilitated the investigation of the dimerization of the diaqua species.

Experimental Section

Materials. All materials were of reagent grade quality and were used without further purification. Deuterium oxide was purchased from Aldrich Chemical Co., Milwaukee, WI, and was at least 99.5 atom % ^{2}H.

Preparation of Ligands. *N,N*-β-Alaninediacetic Acid (β-H₃alada). The method reported by Uehara et al.[4] was used to synthesize this ligand.

Deuterated Nitrilotriacetic Acid (H₃nta-*d*₆). This ligand was prepared by deuteration of *trans*(*N*)-K[Co(gly)(nta)]·2H$_2$O,[10] followed by its decomposition with hydrogen sulfide. In an Erlenmeyer flask equipped with a drying agent, 5.4 g of *trans*(*N*)-K[Co(gly)(nta)]·2H$_2$O was dissolved in 20 mL of ^{2}H$_2$O. The p^{2}H of the solution was adjusted to 10.0 by addition of solid K$_2$CO$_3$, and then 0.2 g of activated charcoal (Norit A, neutral) was added to the solution. The mixture was allowed to stand at 40 °C with stirring until the ^{1}H NMR signals of the methylene protons of the coordinated nta were almost undetectable (ca. 10 h). During the reaction the p^{2}H of the solution was adjusted to 9.5–10.0 by addition of solid K$_2$CO$_3$. The charcoal was removed by filtration and washed with hot water until the washings were colorless. Hydrogen sulfide was bubbled into the combined filtrate and washings until the supernatant solution of the resulting mixture became pale violet. The cobalt sulfide that precipitated was removed by filtration and washed with water. Then the combined filtrate and washings were concentrated to ca. 30 mL on a steam bath, and a small amount of insoluble material was removed by filtration. The pH of the filtrate was adjusted to 1.4 by addition of concentrated HCl, and the desired acid that deposited was collected by filtration and washed with water. Recrystallization was achieved by dissolving the acid (2.4 g) in 20 mL of water at 80 °C by addition of solid K$_2$CO$_3$ and then adding concentrated HCl dropwise until the pH of the solution became 1.4. Yield: 2.3 g (86%). The extent of deuteration of H$_3$nta-d_6 was estimated to be 94% on the basis of the ^{1}H NMR spectrum, which was measured on a sample that contained a known amount of β-alanine as a standard.

Deuterated *N,N*-β-Alaninediacetic Acid (β-H₃alada-*d*₄). This ligand was obtained by a method similar to that described for the preparation of H$_3$nta-d_6 by using racemic *unsym,trans*(*N*)-NH$_4$[Co(β-alada)(gly)]·H$_2$O. Although the racemic complex was not obtained as a crystalline salt in a previous study,[9] in the present work, the complex was obtained as crystals by changing the cation from potassium to ammonium. Anal. Calcd for NH$_4$[Co(β-alada)(gly)]·H$_2$O: C, 29.12; H, 4.89; N, 11.32. Found: C, 29.01; N, 4.89; N, 11.34. Deuteration led to exchange of the four methylene protons on the acetate groups of β-H$_3$alada. The extent of deuteration was estimated to be 78% on the basis of its ^{1}H NMR spectrum.

Preparation of Chromium(III) Complexes. The syntheses described are for complexes containing nondeuterated ligands. The deuterated complexes were synthesized by the same method except the increase in molecular weight was taken into consideration. The final products were air-dried at room temperature.

K₂[Cr(nta)(OH)]₂·4H₂O and Li₂[Cr(nta)(OH)]₂·2H₂O. The potassium salt of the complex was prepared by a modification of the method employed for the corresponding *N,N*-(*S*)-leucinediacetato complex.[2] To a stirred solution of 5 g (20 mmol) of CrCl$_3$·6H$_2$O in 50 mL of water was added 3.8 g (20 mmol) of H$_3$nta. The mixture was boiled gently for 10 min (the H$_3$nta dissolved at 95 °C). The color of the solution changed from green to blue-violet. After the solution was cooled to room temperature, 5.5 g (40 mmol) of K$_2$CO$_3$ was gradually added with stirring. The solution was then concentrated on a steam bath to near dryness. After addition of a small amount of water, the crystals which deposited were filtered and washed with a small amount of water and then water/methanol (1:1) until the washings were free of chloride ion. Fine purple crystals were obtained by dissolving the product in boiling water, cooling, and then adding a small amount of ethanol. Yield: 5.6 g (84%). The lithium salt of the complex was obtained by passing a saturated solution of the potassium salt through a column of cation-exchange resin (Dowex 50W-X8, Li$^+$ form). To the concentrated solution of the eluate was added ethanol until cloudiness persisted, and the solution was cooled in a refrigerator. The green granular crystals were filtered and recrystallized from water by adding ethanol. The potassium salt is slightly soluble and the lithium salt is very soluble in water. The lithium salt was used to obtain spectral data. Crystals of the potassium and lithium salts have different colors in the solid state but give the same green-blue color in solution.

K[Cr(acac)(nta)]·H₂O. This complex was prepared by a modification of the method described in the literature.[3] One-half gram (0.75 mmol) of K$_2$[Cr(nta)(OH)]$_2$·4H$_2$O was substituted for the corresponding ammonium salt as starting material, and no adjustment of the reaction pH was made. The violet reaction solution was loaded onto a column (20 × 300 mm) of QAE-Sephadex A-25, Cl$^-$ form. After the column had been washed with water, the adsorbed band was eluted with 0.14 M aqueous KCl. Only one violet band was eluted, and the eluate was concentrated at 30 °C to near dryness on a rotary evaporator. The KCl which deposited was removed by filtration. A small amount of ethanol was added to the filtrate, and KCl was again removed. After concentration and removal of KCl several more times, granular crystals of the desired complex formed and were collected by filtration. Additional crops of the complex were obtained by treating the final filtrate in a similar fashion. The complexes obtained were combined and recrystallized from warm water by adding ethanol and then acetone until the solution became cloudy. Yield: 0.50 g (85%).

K₂[Cr(mal)(nta)]·2H₂O. Malonic acid (0.31 g, 3.0 mmol) was dissolved in 2.5 mL of water containing 0.13 g (2.0 mmol) of KOH (85%) and 0.5 g (1.5 mmol) of K$_2$[Cr(nta)(OH)]$_2$·4H$_2$O. The mixture was heated on a steam bath at 70 °C for 0.5 h, and the purple solution obtained was loaded onto a column (20 × 300 mm) of QAE-Sephadex (A-25, Cl$^-$ form). After the column was washed with water, the adsorbed band was eluted with aqueous 0.3 M KCl. Two colored bands, the desired purple complex and a trace amount of a blue-violet species, were eluted separately in this order. The purple eluate was concentrated to near dryness and the contaminant KCl was removed as described for the acac complex above. The violet platelike crystals were recrystallized from warm water by adding methanol. Yield: 0.61 g (88%).

K₂[Cr(nta)(ox)]. Oxalic acid dihydrate (0.38 g, 3.0 mmol) was dissolved in 2.5 mL of an aqueous solution containing 0.34 g (5.5 mmol) of KOH (85%) and 0.5 g (0.75 mmol) of K$_2$[Cr(nta)(OH)]$_2$·4H$_2$O. The mixture was heated at 70 °C for 30 min with stirring. The resulting violet solution was loaded onto a column (20 × 300 mm) of QAE-Sephadex (A-25, Cl$^-$ form). After the column was washed with water, the adsorbed band was eluted with 0.3 M aqueous KCl. A large violet band was eluted separately from several small colored bands. The violet eluate was concentrated to near dryness and the contaminant KCl was removed by a method similar to that employed for the acac complex above. The violet scalelike crsytals were recrystallized from warm water by adding methanol. Yield: 0.43 g (71%).

***unsym*-[Cr(β-alada)(H₂O)₂]·H₂O.** This complex was prepared by a modification of the method in the literature.[5] To a solution of 5.3 g (20 mmol) of CrCl$_3$·6H$_2$O in 50 mL of water was added 4.2 g (20 mmol) of β-H$_3$alada, and the mixture was heated at 90 °C for 10 min. In this procedure the ligand dissolved at ca. 60 °C, and the color of the solution changed from green to purple via dark blue. After the solution (pH ~0.1) had been allowed to stand at room temperature, a small amount of the desired reddish purple crystals began to crystallize. Then a saturated aqueous solution of 3.6 g (26 mmol) of K$_2$CO$_3$ was added dropwise for 30 min with stirring. The crystal deposition increased with addition of the aqueous K$_2$CO$_3$. The mixture was concentrated on a steam bath to ca. 20 mL. After the mixture was cooled to room temperature, the crystals were filtered and washed with a small amount of water and then

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(24) Since the line widths observed are 2–3 orders of magnitude larger than the ^{2}H–^{2}H or ^{2}H–^{1}H coupling constants, nuclear spin–spin couplings are not observed and the spectra behave as though they are zero order. As a consequence, only one resonance should be observed for each symmetrically distinct deuteron or set of deuterons: Harris, R. K.; Mann, B. E. *NMR and The Periodic Table*; Academic: London, 1978; p 107 and references therein.

Table I. Elemental Analysis of $[Cr(N(\text{–}O)_3)(O\text{-}O)]^n$ Complexes

complex	% anal.					
	C		H		N	
	calcd	found	calcd	found	calcd	found
$K_2[Cr(nta)(OH)]_2{\cdot}4H_2O$	21.69	21.64	3.34	3.23	4.22	4.28
$Li_2[Cr(nta)(OH)]_2{\cdot}2H_2O$	25.55	25.79	3.22	3.44	4.97	4.97
$K[Cr(nta)(acac)]{\cdot}H_2O$	33.34	33.53	3.81	3.86	3.53	3.67
$K_2[Cr(nta)(mal)]{\cdot}2H_2O$	23.69	24.03	2.65	2.87	3.07	2.89
$K_2[Cr(nta)(ox)]$	23.65	23.69	1.49	1.49	3.45	3.48
unsym-$[Cr(\beta\text{-alada})(H_2O)_2]{\cdot}H_2O$	27.28	27.09	4.58	4.71	4.55	4.57
unsym-$K[Cr(\beta\text{-alada})(acac)]{\cdot}H_2O$ (isomer i)	35.12	34.86	4.42	4.59	3.41	3.21
sym-$K[Cr(\beta\text{-alada})(acac)]$ (isomer ii)	36.74	36.98	3.85	3.92	3.57	3.68
unsym-$K_2[Cr(\beta\text{-alada})(mal)]{\cdot}3.5H_2O$ (isomer i)	24.15	24.24	3.44	3.47	2.82	2.70
sym-$K_2[Cr(\beta\text{-alada})(mal)]{\cdot}H_2O$ (isomer ii)	26.55	26.45	2.67	2.74	3.10	3.04
unsym-$K_2[Cr(\beta\text{-alada})(ox)]{\cdot}H_2O$ (isomer i)	24.66	24.77	2.30	2.38	3.20	3.22

Table II. Deuteron NMR Spectral Data of $[Cr(N(\text{–}O)_3)(O\text{–}O)]^n$ Complexes

complex	δ^a				rel integration
$[Cr(nta\text{-}d_6)(OH)]_2^{2-}$	–26	–13	–7		1:1:1
$[Cr(nta\text{-}d_6)(H_2O)_2]^b$	–43	–17			2:1
$[Cr(nta\text{-}d_6(acac)]^-$	–32	–25	–9		1:1:1
$[Cr(nta\text{-}d_6)(mal)]^{2-}$	–34	–32	–12		1:1:1
$[Cr(nta)(mal\text{-}d_2)]^{2-\,d}$	+31				
$[Cr(nta\text{-}d_6)(ox)]^{2-}$	–31	–27	–15		1:1:1
unsym-$[Cr(\beta\text{-alada-}d_4)(H_2O)_2]^{d,e}$	–62	–39	–33	–10	1:1:1:1
unsym-$[Cr(\beta\text{-alada-}d_4)(acac)]^{-\,b}$	–48	–29	–22	–3	1:1:1:1
sym-$[Cr(\beta\text{-alada-}d_4)(acac)]^{-\,b}$	–42	–5			1:1
unsym-$[Cr(\beta\text{-alada-}d_4)(mal)]^{2-\,b}$	–47	–30	–27	–6	1:1:1:1
unsym-$[Cr(\beta\text{-alada})(mal\text{-}d_2)]^{2-\,b,d}$	+29	+35			1:1
sym-$[Cr(\beta\text{-alada-}d_4)(mal)]^{2-\,b}$	–48	–8			1:1
sym-$[Cr(\beta\text{-alada})(mal\text{-}d_2)]^{2-\,b,d}$	+29				
unsym-$[Cr(\beta\text{-alada-}d_4)(ox)]^{2-\,b}$	–42	–35	–17	–9	1:1:1:1

[a] Relative to Me_4Si. [b] Data obtained immediately after dissolution in H_2O. [c] Data obtained by dissolving a known quantity of the dimer in 0.1 M $HClO_4$ (see text). [d] In 1 mM $HClO_4$. [e] Due to the low solubility, data were obtained on a saturated aqueous solution (~10.7 mM).

water/methanol (1:1) until the washings were free of chloride ion. A second crop of material was obtained by combining the filtrate and washings and concentrating on a steam bath. The KCl which deposited was removed by filtration, and the pH of the filtrate was adjusted to 2.0 by addition of K_2CO_3. The solution was concentrated to near dryness and the crystals which deposited were filtered and washed. The combined crops were recrystallized from boiling water by adding ethanol to give red-purple granular crystals on standing at room temperature. Yield: 5.0 g (86%).

***unsym*-K[Cr(acac)(β-alada)]·H₂O (Isomer i) and *sym*-K[Cr(acac)(β-alada)] (Isomer ii).** To 5 mL of water containing 0.22 g (1.6 mmol) of K_2CO_3 was added 1.0 g (3.2 mmol) of $[Cr(\beta\text{-alada})(H_2O)_2]{\cdot}H_2O$. After the mixture had been heated to 60 °C, 0.34 g (3.4 mmol) of 1,3-pentanedione (acac) was added to the blue-violet solution. The solution, which consisted of two layers, was refluxed for 30 min. The resulting violet solution obtained was loaded onto a column (20 × 400 mm) of QAE-Sephadex (A-25, Cl^- form). After the column had been washed with water, the absorbed band was eluted with 0.14 M aqueous KCl. Only one violet band was eluted (two isomers are present as will be shown), and the eluate was concentrated to near dryness on a rotary evaporator. The contaminant KCl was removed by the method described above for the corresponding nta complex. The violet granular crystals obtained were predominantly pure isomer i and were recrystallized from warm water by adding ethanol and then acetone. Yield: 1.1 g (83%).

It was possible to isolate isomer ii from the residue in the isolation of isomer i described above. However, the following method is preferable because of the presence of large quantities of contaminant KCl. In a 500-mL beaker sealed with plastic film, 1.0 g of isomer i was dissolved in 350 mL of 80% aqueous methanol. The solution was stirred and exposed to a 100-W tungsten lamp at a distance of 30 cm overnight. The solution was concentrated to near dryness on a rotary evaporator kept below 20 °C. A small amount of ethanol was added to the residue, and the crystals of isomer i were removed by filtration. Several additional fractions of crystals were obtained by repeating the following procedure. The filtrate volume was reduced to approximately half the original volume, then methanol and ethanol were added, and the solution was cooled in a refrigerator. The fractions containing more than 80% isomer ii were combined and recrystallized several times from water by adding ethanol and acetone until a constant visible absorption spectrum was obtained. Yield: 0.15 g (10%).

***unsym*-K₂[Cr(β-alada)(mal)]·3.5H₂O (Isomer i) and *sym*-K₂[Cr(β-alada)(mal)]·H₂O (Isomer ii).** $[Cr(\beta\text{-alada})(H_2O)_2]{\cdot}H_2O$ (1.0 g, 3.2 mmol) was added to a solution of 0.22 g of K_2CO_3 in 3 mL of water, and the mixture was heated to 60 °C. To the resulting solution was added a solution of 0.67 g (6.4 mmol) of malonic acid and 0.71 g (10.8 mmol) of KOH (85%) in 3 mL of water at 50 °C. The solution was heated on a steam bath at 70 °C for 30 min. The resulting purple solution obtained was loaded onto a column (20 × 400 mm) of QAE-Sephadex (A-25, Cl^- form). After the column was washed with water, the adsorbed band was eluted with 0.3 M aqueous KCl. Two colored bands, the desired products and a trace amount of another purple species, were eluted in this order. The first band was concentrated to near dryness on a rotary evaporator. The contaminant KCl was removed as described for the K[Cr(acac)(nta)] complex above. The purple granular crystals (isomer i) which deposited were recrystallized from water by adding methanol until the solution just turned cloudy. Yield: 1.3 g (81%).

Isolation of isomer ii was accomplished from 1.0 g of isomer i by using the method described for the corresponding acac complex above. Several fractions, which were shown to contain more than 80% of isomer ii, were combined and recrystallized from water by adding methanol and ethanol (1:1). The recrystallization process was repeated until a constant visible absorption curve was obtained. Yield: 0.11 g (10%).

***unsym*-K₂[Cr(β-alada)(ox)]·H₂O (Isomer i).** This complex was obtained by the same method as that used for the synthesis of the corresponding malonato complex described except that 0.81 g (6.4 mmol) of oxalic acid dihydrate was used. The purple reaction solution was chromatographed as described for the malonato complex. A large violet band, which separated cleanly from several small colored bands, was concentrated to near dryness on a rotary evaporator at 25 °C. The contaminate KCl was removed during the concentration and pink scalelike crsytals (isomer i) eventually deposited. The complex was recrystallized from warm water by adding methanol and ethanol (1:1) until cloudiness persisted. Yield: 1.0 g (71%). The presence of the sym isomer in the filtrate was indicated by ^2H NMR, but it could not be isolated in crystalline form.

Preparation of the Complexes with Deuterated Malonate (mal-*d*₂). For the nta complex, 0.5 g of the complex was dissolved in 3 mL of ^2H_2O and the solution was allowed to stand for ca. 10 h at room temperature. The deuterated complex was obtained by adding methanol and ethanol (1:1) to the solution until it just turned cloudy. The β-alada complexes were deuterated by the same method as that used for the nta complex except 1.5 g of complex was used. From the resulting solution, the deuterated unsymmetrical and symmetrical isomers were isolated and purified by fractional crystallization in 1 mM $HClO_4$.

Table III. Electronic Absorption Spectral Data of $[Cr(N(-O)_3)(O\text{-}O)]^n$ Complexes

	abs max[a] λ/nm (ϵ/M^{-1} cm^{-1})	
complex	I	II
$[Cr(nta)(OH)]_2^{2-}$	585 (157)	409 (200)
$K_2[Cr(nta)(OH)]_2\cdot 4H_2O$[b]	552 (...)	403 (...)
$Li_2[Cr(nta)(OH)]_2\cdot 2H_2O$[b]	613 (...)	414 (...)
$[Cr(nta)(H_2O)_2]$[c]	556 (94)	404 (99)
$[Cr(nta)(acac)]^-$	555 (97)	415 (122 sh)
		392 (206 sh)
		385 (209)
$[Cr(nta)(mal)]^{2-}$	567 (91)	399 (87)
$[Cr(nta)(ox)]^{2-}$	560 (90)	397 (99)
unsym-$[Cr(\beta\text{-alada})(H_2O)_2]$[d]	545 (107)	399 (79)
unsym-$[Cr(\beta\text{-alada})(acac)]^-$	537 (99)	414 (107 sh)
		401 (188 sh)
		384 (192)
sym-$[Cr(\beta\text{-alada})(acac)]^-$	553 (112)	412 (128 sh)
		391 (184)
		385 (181 sh)
unsym-$[Cr(\beta\text{-alada})(mal)]^{2-}$	545 (97)	397 (68)
sym-$[Cr(\beta\text{-alada})(mal)]^{2-}$	558 (107)	405 (87)
unsym-$[Cr(\beta\text{-alada})(ox)]^{2-}$	540 (98)	395 (77)

[a] sh denotes shoulder. [b] Diffuse-reflectance spectrum. [c] Since this complex could not be isolated, the spectrum was obtained by dissolving a known quantity of the dimer in 0.1 M $HClO_4$. [d] In 1 mM $HClO_4$.

Physical Measurements. Analysis. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. The results are summarized in Table I.

Deuteron NMR Spectra. The 31-MHz ^2H NMR spectra were recorded on a Nicolet NT-200WB spectrometer operating at a field of 4.7 T at 20 °C. The instrumentation setup parameters have been described elsewhere.[21] Five milliliters of 50–150 mM solutions in 12-mm tubes were used in the data collection. Data acquisition time was typically 0.3–1 h, depending on the sample concentration. For most samples the free induction decay (FID) signal was multiplied by an exponential decay signal before Fourier transformation to improve the signal to noise ratio. This has the effect of broadening the resonances by 5–10 Hz. The spectral region observed was ±200 ppm with respect to Me_4Si, and an external standard of C^2HCl_3 was assigned to a chemical shift of 7.24 ppm. Upfield shifts are defined as negative. The ^2H NMR data are summarized in Table II.

Electronic Absorption Spectra. The electronic absorption spectra were recorded on a Cary 219 spectrophotometer (Varian Instruments) at ambient temperature and are reported in Table III. The diffuse-reflectance spectra were recorded on a Shimadzu UV-260 spectrophotometer using an integrating-sphere attachment.

Infrared Spectra. Infrared spectra were obtained on a Perkin-Elmer 283B instrument either as Nujol mulls or in ^2H_2O employing AgCl plates. Calibration at 1601 cm^{-1} was performed with a polystyrene standard.

Results and Discussion

$[Cr(nta)(O\text{-}O)]^{n-}$ (O-O = acac, mal, ox) Complexes. The acac and ox complexes have previously been reported by Uehara, et al.[6] and Fuji, et al.[3] In this study the complexes were purified by chromatography as described in the Experimental Section. In contrast to the report,[6] the oxalato complex was found to be quite stable in aqueous solution, and the acetylacetonato complex had somewhat different values for the molar absorptivities (Table III). The ^2H NMR spectra of the nta-d_6 complexes all show three peaks of equivalent intensity (Table II). This pattern is consistent with a structure where nta functions as a quadridentate ligand and the O-O ligand as a bidentate ligand. Fully coordinated nta has two equivalent in-plane acetate rings (G-rings)[25] with chemically inequivalent deuterons and one out-of-plane acetate ring (R-ring) with equivalent deuterons (Figure 1).

The ^2H NMR patterns obtained for the nta complexes would also be expected for a complex where the R-ring acetate ring was uncoordinated. Full coordination of the ligand was confirmed by obtaining the ^2H_2O solution IR spectrum as a function of pH. The carbonyl region was invarient with pH, consistent with full coordination of nta.[26-28] The ^2H NMR spectrum was also invarient over the same pH range. Finally, the elemental analysis for the oxalato complex shows no coordinated water in the solid state (Table I).

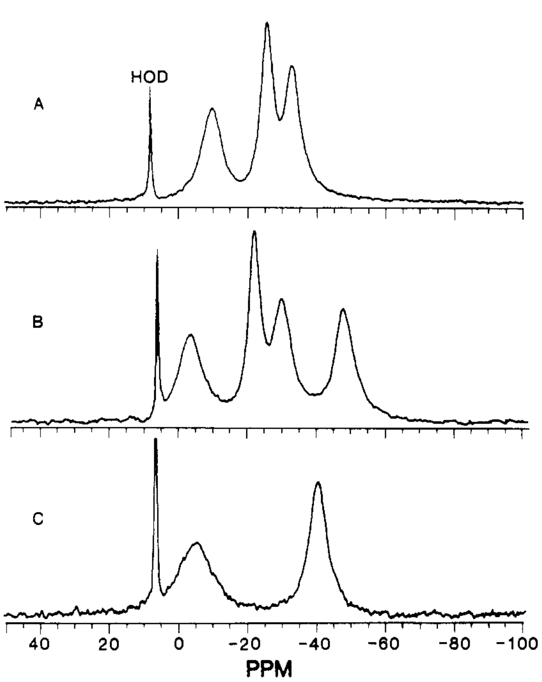

Figure 2. Deuteron NMR spectra: (A) $[Cr(nta\text{-}d_6)(acac)]^-$; (B) *unsym*-$[Cr(\beta\text{-alada-}d_4)(acac)]^-$; (C) *sym*-$[Cr(\beta\text{-alada-}d_4)(acac)]^-$.

$[Cr(\beta\text{-alada})(O\text{-}O)]^{n-}$ (O-O = acac, mal, ox) Complexes. In complexes where β-alada assumes full coordination, two geometrical isomers are possible (Figure 1). In the symmetrical isomer, the six-membered R-ring is coincident with a mirror plane that bisects the G-rings. Since only the two five-membered acetate rings are deuterated, this complex is expected to give rise to two resonances of equal integration value. In the unsymmetrical isomer the two five-membered chelate rings are inequivalent (the complex has C_1 symmetry), and four resonances of equivalent intensity are expected in the ^2H NMR spectrum.

In the synthesis of the acetylacetonato complex two isomers were obtained from the reaction mixture as described in the Experimental Section. The ^2H NMR spectrum gave four resonances (1:1:1:1) for isomer i and two resonances (1:1) for isomer ii, as seen in Figure 2 and Table II. Thus, isomer i and isomer ii can be assigned to the unsymmetrical and symmetrical configurations, respectively. The same structural assignments can be made for the corresponding malonato (isomers i, and ii) and oxalato (isomer i, only) complexes (Table II).

In order to confirm the configurational assignments independently, chelated malonate was deuterated as previously reported.[23] The ^2H NMR spectra of the complexes deuterated on the bidentate ligand only are expected to give rise to one or two signals in the symmetrical and unsymmetrical configurations, respectively. Two signals were indeed observed for isomer i and one signal for isomer ii (Table II) confirming the assignments.

Full coordination of the β-alada chelate was shown by obtaining the ^2H_2O solution IR spectrum in the carbonyl region as a function of pH. The invariance of the IR, ^2H NMR, and UV/vis spectroscopic data over the same pH range supports full coordination

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(25) The R (out-of-plane, relaxed) and G (in-plane, girdling) designations for the chelate rings are those used for the Co(III)–edta chelate system as introduced by: Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549.

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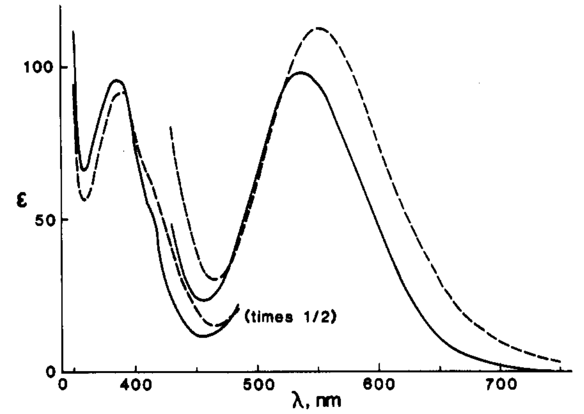

Figure 3. Electron absorption spectra of *unsym*-$[Cr(\beta\text{-alada})(acac)]^-$ (—) and *sym*-$[Cr(\beta\text{-alada})(acac)]^-$ (- - -).

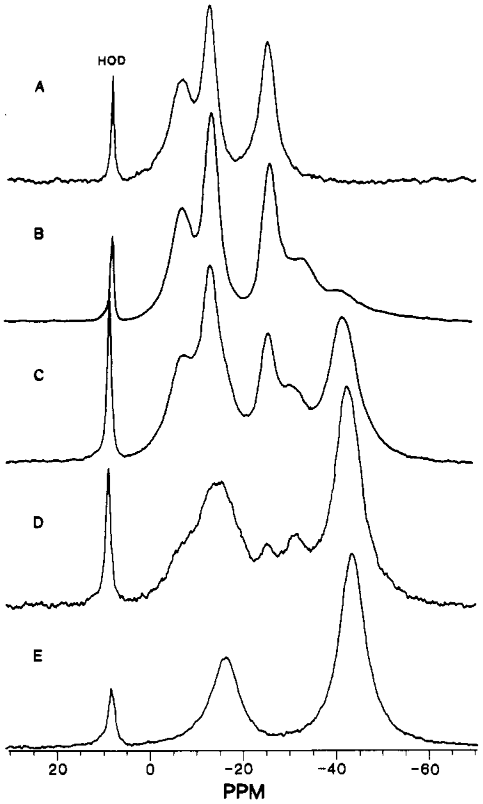

Figure 4. Deuteron NMR spectra of $[Cr(nta\text{-}d_6)(OH)]_2^{2-}$ at (A) pH 7.1, immediately after dissolution, and for equilibrated solutions at (B) pH 6.0, (C) pH 5.3, (D) pH 4.4, and (E) pH 3.5.

of all ligands in the acetylacetonato, malonato, and oxalato complexes.

In the $[Cr(acac)(\beta\text{-alada})]^-$ complex, the unsymmetrical and symmetrical isomers gradually isomerize to an equilibrium distribution at room temperature. The absorption spectra of the pure isomers are shown in Figure 3. Spectra obtained during isomerization exhibit several isosbestic points (524, 473, and 394 nm), indicating the presence of only two species. An equilibrium distribution[29] (K = [unsym]/[sym]) of 4.9 was obtained after allowing the solutions to sit for several days at room temperature in the dark. If the solutions were exposed to light (as described in the Experimental Section), a distribution constant of 0.63 was obtained. Similar behavior was also observed for the corresponding malonato complex. This behavior was utilized for isolation of the less stable symmetrical isomer, as described in the experimental section.

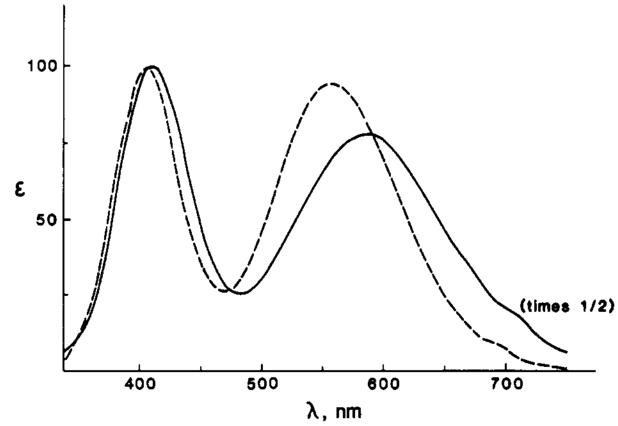

Figure 5. Electronic absorption spectra of $[Cr(nta)(OH)]_2^{2-}$ in H_2O (—) and in 0.1 M $HClO_4$ (- - -).

$[Cr(nta)(OH)]_2^{2-}$. An interesting phenomenon has been reported with respect to the ammonium salt of this complex by Uehara, et al.[5,7] Crystal of two distinctly different colors, which differed only in water content, were isolated. In solution, these crystals gave the same absorption spectrum. The structure of the complex in solution was proposed as being $[Cr(nta)(OH)(H_2O)_2]^-$, where the three nta carboxylates are coordinated facially and the nitrogen is free. They based their assignment primarily on the maximum of the first electronic absorption band, which is at considerably lower energy (585 nm) than that typically observed for mononuclear $CrNO_5$ type complexes.

In order to define the solution structure, the complex was prepared with deuterated nta (nta-d_6) and the ^2H NMR spectrum was measured. The spectrum of the complex obtained immediately after dissolution at pH 7.1, Figure 4A, exhibits three resonances of equal integration value. This indicates that there are three different environments for the deuterons on the nta-d_6 ligand. The structure proposed by Uehara et al. has C_{3v} symmetry on the NMR time scale (assumes rapid proton exchange at the OH^-/H_2O sites), and all deuterons are equivalent. This is not consistent with the ^2H NMR data. The ^2H NMR data are in agreement with the structure $[Cr(nta)X_2]^n$ where nta is fully coordinated (C_s symmetry) (Figure 1), as observed for the corresponding acac, mal, and ox complexes.

The visible absorption spectral data, however, suggest a structure other than the one proposed. Srdanov et al. confirmed the bis(μ-hydroxo)-bridged binuclear structure for *sym,cis*-$[Cr(edda)(OH)]_2$ by X-ray crystallographic analysis.[13] The first absorption maximum of the edda complex is 23 nm lower in energy than that of the mononuclear diaqua complex, *sym,cis*-$[Cr(edda)(H_2O)_2]^+$.[30] For the nta complex described above, the maximum is shifted 28 nm lower in energy than that observed for the diaqua complex (the characterization of the diaqua complex will be described below), suggesting the possibility of a bis(μ-hydroxo)-bridged binuclear structure (Figure 5). This binuclear structure still maintains the symmetry relationship among the deuterons summarized for the fully coordinated nta mononuclear complex and is, therefore, consistent with the NMR data.

The species undergoes some change on standing at pH 7, as evidenced in the absorption spectrum, reaching equilibrium in 3 h at room temperature. The changes become more pronounced with a decrease in pH as clearly seen in the ^2H NMR spectrum. Spectral data were obtained for the equilibrated solution (as evidenced by the absorption spectrum) at various pHs (Figure 4). In addition to the three resonances observed for the proposed dimer at pH 7.1 (Figure 4A), new resonances grow in as the pH is lowered (Figure 4B–D). The spectrum at pH 3.5 consists of two single resonances at −17 and −44 ppm, which integrate 1:2 (Figure 4E). The formation of binuclear complexes from monomers of Cr(III) and Co(III) is well-known.[8,11–18,31] Accordingly,

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(29) Isomer distribution was estimated from the absorption spectra by using the method of: Hirt, R. C.; King, F. T.; Schmitt, R. G. *Anal. Chem.* **1954**, *26*, 1270.

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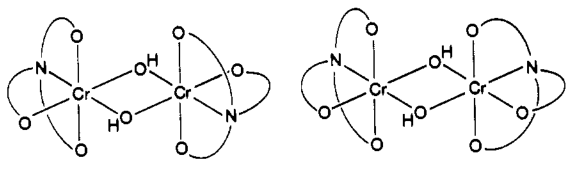
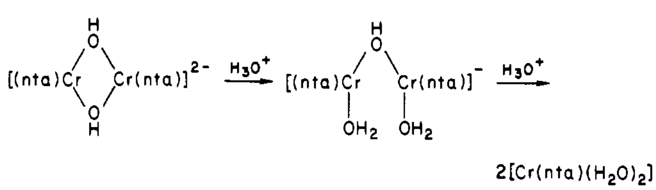


Figure 6. Possible geometric isomers of $[Cr(nta)(OH)]_2^{2-}$.

it seems reasonable that the species present at low pH is the monomer $[Cr(nta)(H_2O)_2]$. However, as only two resonances are observed (three are predicted theoretically, as discussed earlier), there is a coincidence of two resonances. The IR spectrum at pH 1 in ^2H_2O does not show a peak near 1720 cm^{-1}, consistent with the absence of a free carboxylate group[28] and, thus, full coordination of nta.

As seen in Figure 4C,D, at intermediate pHs additional resonances are observed as a shoulder (−8 ppm) and as a peak (−31 ppm), indicating the presence of a third species. These resonances reach a maximum at about pH 4.6 and disappear under more acidic conditions. Unfortunately, there is not enough information to characterize the structure of the intermediate. A possible explanation is given in the following scheme.



This scheme is consistent with the fact that bis(μ-hydroxo)-bridged Cr(III)[14,15,18] and Co(III)[8a,17] complexes are known to undergo acid cleavage of the hydroxo bridges to form mono(μ-hydroxo)-bridged species as intermediates. Formation of a stable hydroxo/aqua-bridged intermediate is also possible.[11] Below pH 3.5, the ^{2}H NMR and absorption spectra are invarient in support of the monomeric diaqua structure. Since the diaqua species could not be isolated as a solid due to its high solubility, quantitative absorption spectral data were obtained by dissolution of a known quantity of the dimer in 0.1 M $HClO_4$. Figure 5 shows the absorption spectra for the mononuclear and binuclear species. The similarity of the absorption spectrum obtained for $[Cr(nta)(H_2O)_2]$ to the spectra obtained for other mononuclear NO_5 complexes (Table III) is consistent with the formulated structure.

There are two isomers possible for the bis(μ-hyhdroxo)–nta complex (Figure 6). In both isomers the mononuclear components are symmetry-related, and thus a maximum of three resonances would be expected for each. If both isomers were present, more than three resonances and possibly as many as six would be expected unless there was the unlikely possibility that the two sets of resonances would be totally accidentally degenerate. Since only one set is observed (Figure 4A), it is very likely that only one isomer of the dimer is present although it is not possible to assign the particular structure. Furthermore, careful chromatography on QAE-Sephadex (A-25, Cl$^-$ form) indicates that the solution contains only one species. Only one isomer has been isolated for similar bis(μ-hydroxo) binuclear complexes, such as the chromium(III) complex with (*S*)-alanine.[12]

***unsym*-[Cr(β-alada)$(H_2O)_2$].** This complex has previously been reported by Uehara et al. and assigned as the diaqua structure in solution.[5] However, they did not consider the two possible geometric isomers (Figure 1). Figure 7 and Table II show the ^{2}H NMR data of the complex in 1 mM $HClO_4$, and Table III contains the absorption spectral data. The ^{2}H NMR spectrum consists of four resonances with equivalent integration values consistent with the unsymmetrical structure as previously discussed. The complex is easily crystallized, and the absorption spectra of crystalline fractions were invarient, indicating that the complex is a single species. The ^{2}H NMR and absorption spectra showed no changes after the complex sat for several days at room temperature in acid solution. Furthermore, the complex showed only a very small change in the absorption spectrum after being heated in solution with activated charcoal at 85 °C for 1 h. Thus, the unsymmetrical isomer is more thermodynamically stable, and stereoselectivity between isomers is higher than that in the corresponding acac, mal, and ox complexes.

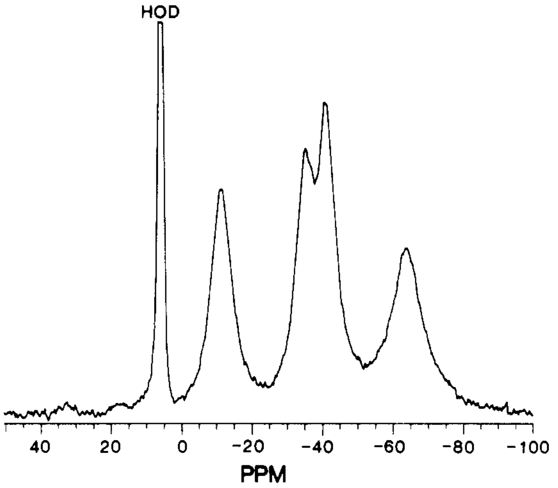


Figure 7. Deuteron NMR spectrum of $[Cr(\beta\text{-alada-}d_4)(H_2O)_2]$ in 1 mM $HClO_4$.

As expected, *unsym*-[Cr(β-alada)$(H_2O)_2$] exhibits spectral behavior parallel to that observed for $[Cr(nta)(H_2O)_2]$ as a solution of the complex is made basic. There is a shift in the maximum of the low-energy electronic absorption band from 545 to 557 nm, and the ^{2}H NMR spectrum undergoes a major change. The four resonances observed in acidic solution (Table II) decrease to give rise to a complex multiline spectrum, which resolves into a new four line spectrum (−1, −88 −24, −37 ppm; 1:1:1:1 relative integration values) as the pH is increased. This behavior is consistent with formation of a bis(μ-hydroxo)-bridged species at high pH as observed for $[Cr(nta)(H_2O)_2]$. Again, the NMR spectrum at intermediate pH values is too complex to establish the nature of any intermediate(s).

In the solid state, another structure, [Cr(β-Halada)(OH)$(H_2O)_2$], which has an uncoordinated carboxylic acid group hydrogen bonded with the hydroxo ligand, has been proposed.[7] The assignment is based on the presence of an IR peak at 1690 cm^{-1} and the disappearance of this peak after heating at 160 °C. A peak at 1678 cm^{-1} was found in our measurements. This value is in agreement with those reported for other chromium(III)[3] and cobalt(III)[32] complexes having all carboxylates coordinated. Furthermore, the complex crystallizes under strong acid conditions (pH $\approx$0) as described in the Experimental Section. An aqua/hydroxo compelx is unlikely to form under these conditions. Accordingly, it is reasonable to assign the same structure in the solid state as that found in solution.

Color Variation of $[Cr(nta)(OH)]_2^{2-}$ Salts. Two kinds of crystals (violet and green) have been reported for the ammonium salt of $[Cr(nta)(OH)]_2^{2-}$ by Uehara et al.[5,7] In the present work, violet crystals were isolated for the potassium salt and green crystals for the lithium salt. These complexes, including the ammonium salts, show the same absorption spectra in solution. Furthermore, the absorption maxima of the diffuse-reflectance spectra of both potassium and lithium salts are clearly different from those in solution (Table III). Due to the stereoselectivity found for the binulear complex in solution, it seems unlikely that this color variation in the solid state is due to isomerism. Although similar color variations in solids have been reported for chromium(III) and cobalt(III) complexes with 2,2′-bipyridine and 1,10-phenanthroline, no explanation was given.[33] This interesting phenomenon is currently under investigation. Preliminary magnetic susceptibility measurements (4.5 K) of the lithium and potassium salts show that both complexes have binuclear structures.

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Summary. It has been shown that the tripodlike amine tricarboxylate ligands, nta and *β*-alada, coordinate as quadridentate chelating agents to Cr(III), not as terdentate ligands with the amine free as previously reported. Absorption spectral changes which had been ascribed to ter-/quadridentate changes in coordination are, in fact, associated with dimer formation instead, where cis-coordinated waters in the monomers are replaced by bridging hydroxides in the dimers. The conclusions reached in this study are consistent with previously reported studies of the corresponding Co(III)–nta complex. Deuteron NMR spectroscopy was instrumental to the study of the mode of ligand coordination and the dimerization process.

Acknowledgment. The authors thank D. Appel for his continuing help in obtaining NMR data. Acknowledgment is made to W. D. Wheeler and C. A. Green for helpful discussions. This study was partially supported by the USDA (Grant No. 82-CRCR-1-1005) and NIH (Grant No. GM 23081). The Nicolet NT-200WB was acquired with the assistance of the Boeing Corp.

Registry No. $K_2[Cr(nta)(OH)]_2$, 38122-55-3; $Li_2[Cr(nta)(OH)]_2$, 102539-13-9; K[Cr(nta)(acac)], 102628-85-3; $K_2[Cr(nta)(mal)]$, 102539-14-0; $K_2[Cr(nta)(ox)]$, 102629-49-2; *unsym*-[Cr(*β*-alada)$(H_2O)_2$], 26268-77-9; *unsym*-K[Cr(*β*-alada)(acac)], 102539-15-1; *sym*-K[Cr(*β*-alada)(acac)], 102628-86-4; *unsym*-K_2[Cr(*β*-alada)(mal)], 102539-16-2; *sym*-K_2[Cr(*β*-alada)(mal)], 102628-87-5; *unsym*-K_2[Cr(*β*-alada)(ox)], 102575-54-2; Cr(nta)(H_2O), 18042-08-5; H_3nta-d_6, 102539-17-3; *trans*-(*N*)-K[Co(gly)(nta)], 23242-64-0; *β*-H_3alada-d_4, 102539-18-4; *unsym,trans*(*N*)-NH_4[Co(*β*-alada)(gly)], 102628-88-6; D_2, 7782-39-0.

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Conformational Characterization of the Stereoisomers of a Nickel(II) Macrocyclic Tetraamine Complex

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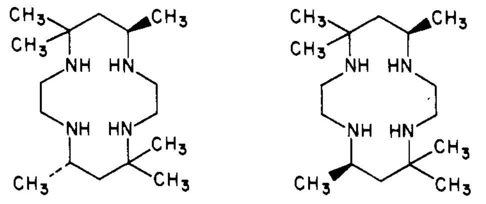
Received July 18, 1985

Six stereoisomers of the complex (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) have been prepared, characterized, and shown to be derived from variations in the configurations of the two asymmetric carbon centers and the four asymmetric nitrogen centers. The assignments of structures to these isomers have been accomplished by means of thorough stereochemical analysis combined with proton magnetic resonance and infrared spectral data of these species. The relative energies of these species are discussed in terms of the conformational energies of the chelate ring systems and methyl substituent interaction energies.

Introduction

In a previous paper[1] we reported the stereochemistry of the diastereoisomers of the complex (5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II), $[Ni(1,4\text{-}CTH)]^{2+}$. This paper concerns the diastereoisomers of the nickel(II) complexes of *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *meso*-1,7-CTH or tet a, and *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *rac*-1,7-CTH or tet b (Chart I). The complex ion $[Ni(1,7\text{-}CTH)]^{2+}$ can exist in 20 theoretically possible diastereoisomeric forms, depending on the configurations of the two asymmetric carbon centers and the four asymmetric nitrogen centers. Four of these diastereoisomers, Ni(*β-meso*-1,7-CTH)$(ClO_4)_2$, Ni(*α-rac*-1,7-CTH)$(ClO_4)_2$, Ni(*β-rac*-1,7-CTH)$(ClO_4)_2$, and Ni(*γ-rac*-1,7-CTH)$(ClO_4)_2$, have been prepared, and their X-ray crystal structures have been reported by Curtis et al.[2-4] In this work, two new stereoisomers of this complex, the *δ* and the *ϵ* diastereoisomers, were prepared. The electronic, infrared, and proton magnetic resonance spectra, as well as the stereochemistry of these six isomers in solution, were investigated.

Chart I



I
tet a or *meso*-1,7-CTH

II
tet b or *rac*-1,7-CTH

Experimental Section

Reagents. Ni(*β-meso*-1,7-CTH)$(ClO_4)_2$, Ni(*α-rac*-1,7-CTH)$(ClO_4)_2$, Ni(*β-rac*-1,7-CTH)$(ClO_4)_2$, and Ni(*γ-rac*-1,7-CTH)$(ClO_4)_2$. These complexes were prepared by using the reported procedures.[3-6]

Ni(*δ-rac*-1,7-CTH)$(ClO_4)_2$. A 0.5-g sample of Ni(*α-rac*-1,7-CTH)$(ClO_4)_2$ was dissolved in 100 mL of water at 80 °C that had been acidified with a few drops of 70% $HClO_4$, and then 4 drops of diluted aqueous ammonia was added. This solution was still acidic. After the solution was cooled, a yellow product crystallized. This product was filtered and dried in vacuo. Anal. Calcd for $C_{16}H_{36}N_4NiCl_2O_8$: C, 35.45; H, 6.69; N, 10.34. Found: 35.50; H, 6.63; N, 10.26.

Ni(*ϵ-rac*-1,7-CTH)$(ClO_4)_2$. The isomer was prepared by stirring at room temperature 0.5 g of Ni(*α-rac*-1,7-CTH)$(ClO_4)_2$ in 100 mL of diluted aqueous ammonia. An excess of sodium perchlorate was added; the orange product precipitated. This product was filtered, washed with water, ethanol, and ether, and then dried in vacuo. Anal. Calcd for $C_{16}H_{36}N_4NiCl_2O_8$: C, 35.45; H, 6.69; N, 10.34. Found: C, 35.42; H, 6.51; N, 10.28.

Ni(*β-meso*-1,7-CTH)Cl_2, Ni(*β-meso*-1,7-CTH)$(NCS)_2$, Ni(*α-rac*-1,7-CTH)$(NCS)_2$, Ni(*β-rac*-1,7-CTH)$(NCS)_2$, and Ni(*γ-rac*-1,7-CTH)$(NCS)_2$. These complexes were prepared by using the methods described by Ito and Toriumi,[7] Warner and Busch,[6] and Dei.[8]

Ni(*α-rac*-1,7-CTH)Cl_2. This derivative was prepared by stirring 4 g of Ni(*α-rac*-1,7-CTH)$(ClO_4)_2$ in 100 mL of 0.1 N HCl to which 10 g of NaCl had been added. An insoluble blue material formed immediately. The mixture was stirred for 1 h, and the product was isolated by filtration and dried in vacuo. Anal. Calcd for $C_{16}H_{36}N_4NiCl_2$: C, 46.41; H, 8.76; N, 13.53. Found: C, 46.42; H, 8.79; N, 13.55.

Ni(*δ-rac*-1,7-CTH)Cl_2. This derivative was prepared from Ni(*δ-rac*-1,7-CTH)$(ClO_4)_2$ by following the same procedure described above for

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