

Figure 1. FT IR diffuse-reflectance ratio spectra. The upper curve is $\text{Ni}(i\text{-PrDTP})_2\text{-Na}^+\text{-X/Na}^+\text{-X}$; the lower curve is $\text{Ni}(i\text{-PrDTP})_2\text{-HiSil 233/HiSil 233}$.

X-ray powder diffraction patterns of dehumidified $\text{Ni}(i\text{-PrDTP})_2\text{-Na}^+\text{-X}$ pigment indicated large losses of intensity in the low-angle diffraction maxima, which are influenced by intracage perturbations,¹⁵ and a unit cell size increase by nearly 0.05 Å relative to that for the zeolite treated only with solvent and dried similarly. The X-ray parameters returned to normal when the anchored complex was allowed to react with 1 N $\text{NaOH}(\text{aq})$ at 90 °C, which resulted in stripping of most of the nickel. BET surface area was also reversibly reduced in the pigment although it can be argued that pore blockage by external surface-anchored molecules could similarly reduce nitrogen adsorption. Reaction of excess $\text{Ni}(i\text{-PrDTP})_2$ with $\text{Na}^+\text{-A}$ zeolite resulted only in trace adsorption of the nickel species by the solid ($\leq 0.02\%$ Ni). $\text{Na}^+\text{-A}$ cages are too small to admit the complex²⁵ but exhibit an external surface similar to that of $\text{Na}^+\text{-X}$. An estimate of maximum external surface anchoring can be made from the analysis of the reaction product between a large excess of $\text{Ni}(i\text{-BuPhODTP})_2$ and $\text{Na}^+\text{-X}$. A pale yellow solid was isolated which contained only 0.34% Ni.

In compounds with the P-O-C linkage, characteristic IR bands are found in the regions 1065-905 and 875-730 cm^{-1} assignable to (P)-O-C stretching modes and to P-O-(C) stretching modes, respectively.^{17,26} Generally speaking, these bands would be expected to shift to lower frequencies upon substitution of a silicon (or aluminum) atom from the zeolite framework for carbon. Comparison of the room-temperature FT IR diffuse-reflectance ratio spectrum of $\text{Ni}(i\text{-PrDTP})_2$ supported on silica gel vs. silica gel with that of the complex on $\text{Na}^+\text{-X}$ vs. the $\text{Na}^+\text{-X}$ support phase reveals striking differences in regions assignable to P-S and P-O stretching modes¹⁹ (Figure 1). The $\text{Na}^+\text{-X}$ -supported complex shows additional structure, most notably two bands at 1038 and 886 cm^{-1} . Also, the relative intensity of the very strong band at 960 cm^{-1} for $\text{Ni}(i\text{-PrDTP})_2$ on SiO_2 gel (possibly C-C stretch) is reduced in the zeolite phase. The 886- cm^{-1} band is reasonably assigned to a P-O-T (T = Al, Si of zeolite framework) stretching vibration, lower in energy than the corresponding antisymmetric P-O-C modes,¹⁷ and probably diagnostic of the anchoring linkage.

Diffuse-reflectance electronic difference spectra of the supported complex (vs. those of the respective supports) showed blue shifts of the two ligand field bands on $\text{Na}^+\text{-X}$ or $\text{Na}^+\text{-NH}_4^+\text{-X}$ ($\bar{\nu}_1 = 15.4 \times 10^3 \text{ cm}^{-1}$, $\bar{\nu}_2 = 19.4 \times 10^3 \text{ cm}^{-1}$) compared to HiSil 233 supported species or to the complex in fluid CCl_4 solution ($\bar{\nu}_1 = 14.5 \times 10^3 \text{ cm}^{-1}$, $\bar{\nu}_2 = 19.1 \times 10^3 \text{ cm}^{-1}$). Porta has shown a correlation between the $\bar{\nu}_1$ spectral frequency

of the NiS_4 square-planar chromophore and the Ni-S bond distance.²⁷ Specifically, as more electron donation from sulfur to nickel occurs, the bond order increases and the $\bar{\nu}_1$ band shifts to higher frequency. From Porta's correlation,²⁷ one may estimate the Ni-S bond distance in the $\text{Na}^+\text{-X}$ -encapsulated species to be ca. 2.215 Å as compared to 2.233 Å for the HiSil 233 supported or free complex.

The nickel complex is potentially deactivated toward adduct formation in the zeolite system as a consequence of enhanced electron donation by sulfur into the nonbonding p orbital of nickel. Experimentally, it can be shown that adducts with primary amines do not readily form for the zeolite-encapsulated species but are observed with the HiSil 233 supported complex and are known to occur with unsupported compounds or in solution.^{17,18} Our original goal of activating such adducts toward further reactions consequently was not achieved.

To gauge thermal stability, differential thermal analysis of the $\text{Ni}(i\text{-PrDTP})_2$ complex in $\text{Na}^+\text{-X}$ was performed under flowing N_2 and compared to an analysis of the pure zeolite substrate. A sharp exothermic peak centered at 290 °C superimposed onto the broad endothermic silica loss peak for the $\text{Na}^+\text{-X}$ substrate was observed. The silica gel support system yielded a much broader decomposition curve between 150 and 320 °C for the complex; apparently the zeolite-supported complex exhibits a higher threshold decomposition temperature, which may reflect a hindrance of the alkene elimination reaction thought to operate during the thermal decomposition of metal dithiophosphates.²⁸ Despite its apparent thermal stability, the $\text{Ni}(\text{DTP})_2\text{-Na}^+\text{-X}$ pigment exhibits the characteristic pungent odor of the ligand system after several weeks of storage at room temperature indicative of some, if minor, decomposition.

Acknowledgment. We thank Professor J. San Fillipo for measurement of the FT IR spectra, Dr. Eric Stern for helpful discussions, and Engelhard Corp. for permission to publish this work.

Contribution from the Chemistry Department,
Bucknell University, Lewisburg, Pennsylvania 17837

cis- and *trans*- $[(\text{en})_2\text{Co}(\text{NO}_2)(\text{C}_2\text{O}_4)]$, Cobalt(III) Complexes Containing a Monodentate Oxalato Ligand

J. N. Cooper,* C. A. Pennell, and B. C. Johnson

Received November 17, 1982

Anations of *cis*- and *trans*- $[(\text{en})_2\text{Co}(\text{H}_2\text{O})(\text{NO}_2)]^{2+}$ with nitrate and thiocyanate are stereoretentive,¹ and the *cis* isomer aquates slowly in acid solutions at elevated temperatures.² These reports prompted us to use anation of the aqua-nitrito-*N* complexes with dinegative, potentially bidentate ligands to compel their monodentate ligation. Although oxalato is well-known both as a monodentate³⁻⁵ and as a bridging^{5a,6} species, it occurs more commonly as a bidentate ligand.⁵ We report here the stereoretentive preparation and characterization

- (1) Basolo, F.; Stone, B. D.; Pearson, R. G. *J. Am. Chem. Soc.* **1953**, *75*, 819.
- (2) Reiter, L. G.; Udovenko, V. V.; Batyushkina, T. V. *Koord. Khim.* **1978**, *4*, 752.
- (3) Saffir, P.; Taube, H. *J. Am. Chem. Soc.* **1960**, *82*, 13.
- (4) Chan, S. C.; Choi, M. C. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1949.
- (5) (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley: New York, 1978; pp 234-237. (b) Brown, P. M.; Harris, G. M. *Inorg. Chem.* **1968**, *7*, 1872.
- (6) Chan, S. C.; Harris, G. M. *Ibid.* **1971**, *10*, 1317.
- (7) Ogino, H.; Tsukahara, K.; Morioka, Y.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1736.

of two new complexes, *cis*- and *trans*-[(en)₂Co(NO₂)(C₂O₄)], containing the monodentate oxalato ligand.

Experimental Section

General Data. Sodium perchlorate, LiCl, and LiClO₄·3H₂O were obtained from G. F. Smith Chemical Co., made up as concentrated solutions for ion-exchange elutions, and filtered before use. Other common chemicals were of reagent grade and were used without further purification. Chromatographic separations were accomplished as previously described⁷ by using Sephadex resins (SP-C-25, Na⁺ form; QAE-Q-25, Cl⁻ form; G-10, to desalt). Elemental analyses of solid samples were performed by Galbraith Laboratories, Inc., Knoxville, TN. Visible-UV spectra were recorded either on a Hitachi 100A or on a Beckman DBG7 spectrophotometer in Milli-Q (Millipore) water; IR spectra were recorded on a Perkin-Elmer 337 in KBr pellets. To deuterate the amines, complexes were dissolved in 99.8% D₂O containing a trace of Na₂C₂O₄ to suppress aquation and hasten exchange and were recrystallized 1–2 days later. pH values were determined on a Beckman 7 Research pH meter using a Sorex semimicro combination glass reference electrode, calibrated against standard buffers. Photolyses were performed on magnetically stirred, thermostated solutions with a 4-W UV lamp from Ultraviolet Products Inc., operated in the long-wavelength mode (λ_{max} 350 nm) and calibrated by ferrioxalate actinometry.⁸

¹³C and ¹H NMR spectra were obtained on a JEOL FX90 Q at 22.50 and 89.55 MHz, respectively, in D₂O. Chemical shifts are reported in ppm downfield from the methyl groups on TSP (2,2-dimethyl-2-silapentanoate, sodium salt), which was the internal reference. The ¹³C spectra were run in the proton-decoupled mode; up to 40 000 pulses were performed for the ¹³C and up to 1000 for the ¹H spectra, depending on the solubility of each complex.

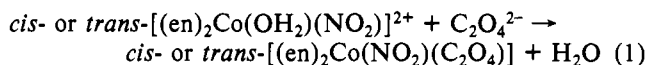
trans-(Oxalato)(nitrito-*N*)bis(ethylenediamine)cobalt(III), trans-[(en)₂Co(NO₂)(C₂O₄)]·2H₂O. The *trans* isomer has been prepared by two routes. In the first preparation, 0.58 g of *trans*-[(en)₂CoCl₂]⁺Cl⁻ was dissolved in 2 mL of H₂O, 0.14 g of NaNO₂ was dissolved in 1 mL of H₂O, and the two solutions were cooled in an ice bath and mixed at 0 °C. After 1 min, a solution of 0.27 g of Na₂C₂O₄ in 10 mL of H₂O, adjusted to pH 6 with HClO₄, was added and the mixture heated to 40–45 °C for 45 min. An uncharacterized pale orange precipitate was filtered and the filtrate passed successively through SP-C-25 (Na⁺ form) and QAE-Q-25 (Cl⁻ form) resins to convert ionic impurities to NaCl. The orange, charge-neutral band was collected and flash evaporated to ca. 10 mL, passed through a G-10 column to desalt, and further flash evaporated to ca. 3 mL. A 12-mL portion of 2-propanol was added dropwise and the precipitation completed upon standing of –10 °C for several hours. Anal. Calcd for [(en)₂Co(NO₂)(C₂O₄)]·2H₂O: C, 20.63; H, 5.73; N, 20.06; Co, 16.91. Found: C, 20.63; H, 5.95; N, 19.92; Co, 16.94. IR spectrum (KBr) (cm⁻¹): oxalato 1585, 1300, 775; nitrito 1420, 1325, 815. UV-vis spectrum: [λ_{max}/nm (ε/M⁻¹ cm⁻¹): 465 (125), 330 (1835), 243 (15830), 202 (19590)]. ¹³C NMR (ppm): oxalato 170.11, 178.34; ethylenediamine 47.46. ¹H NMR (ppm): CH₂ 2.75. The solubility in H₂O at 25 °C was 60 mg/mL. Yields were typically 25%, based on *trans*-[(en)₂CoCl₂]⁺Cl⁻.

In the second route, ice-cold saturated aqueous solutions of *trans*-[(en)₂CoCl₂]⁺Cl⁻ and NaNO₂ were mixed in equivalent proportions and allowed to stand 45 min in an ice bath, and the product, *cis*-[(en)₂Co(Cl)(NO₂)]Cl, was filtered.¹⁰ Addition of saturated NaClO₄ to the filtrate precipitated *trans*-[(en)₂Co(Cl)(NO₂)]ClO₄. In a typical preparation, 0.36 g of the *trans*-[(en)₂Co(Cl)(NO₂)]ClO₄ was allowed to aquate¹¹ in the dark at room temperature in 30 mL of H₂O for 3 h, after which 0.13 g of Na₂C₂O₄ was added and the mixture was stirred until dissolution and stored in the dark overnight. The product was passed through an SP-C-25 column (Na⁺ form) and eluted with H₂O; the charge-neutral *trans* isomer was isolated as above. Yields were typically 65–70%, based on the initial *trans*-[(en)₂Co(Cl)(NO₂)]ClO₄.

cis-(Oxalato)(nitrito-*N*)bis(ethylenediamine)cobalt(III), cis-[(en)₂Co(NO₂)(C₂O₄)]·2H₂O. To prepare the *cis* isomer, 0.30 g of *cis*-[(en)₂Co(Cl)(NO₂)]Cl (see above) was allowed to aquate¹¹ in 15 mL of H₂O in the dark 10–20 h, 0.13 g of Na₂C₂O₄ was added, and the mixture was heated in the dark to 40–45 °C for 2 h. The solution was cooled to room temperature and passed through an SP-C-25 column. Elution with water led to isolation of the dark orange, charge-neutral band, which was flash evaporated to ca. 3 mL. During the evaporation, separation of a dark orange solid began and was completed on standing in an ice bath for 2 h. The solid was filtered, rinsed with ethanol, and air-dried. The solubility in H₂O at 25 °C is ca. 1.5 mg/mL. Anal. Calcd for [(en)₂Co(NO₂)(C₂O₄)]·2H₂O: C, 20.63; H, 5.73; N, 20.06; Co, 16.91. Found: C, 20.42; H, 5.82; N, 20.02; Co, 16.94. IR spectrum (KBr) (cm⁻¹): oxalato 1615, 1305, 775; nitrito 1405, 1340, 825. UV-vis spectrum [λ_{max}/nm (ε/M⁻¹ cm⁻¹): 474 (134), 315 sh (2360), 241 (18 600), 200 (15 700)]. ¹³C NMR (ppm): ethylenediamine 47.94, 47.57, 46.27, 45.99. ¹H NMR (ppm): CH₂ multiplet 2.82–2.54. Yields typically were 35%, based on the *cis*-[(en)₂Co(NO₂)(Cl)]Cl.

Results and Discussion

Preparation and Characterization. The principal synthetic reaction for each isomer is an oxalate anation of the corresponding (nitrito-*N*)aquacobalt(III) cation to produce the corresponding oxalato-nitrito-*N* complex (eq 1) with retention



of configuration. For neither isomer is the reaction quantitative. Essentially complete retention of configuration is also reported in anations of [(en)₂Co(OH₂)(NO₂)]²⁺ with NCS⁻ and NO₂⁻.¹ Dark conditions were maintained during aquation because of the reported photosensitivity¹¹ of the chloro-nitrito-*N* species. The *trans* isomer was readily formed either on gentle heating or on reacting overnight. The principal side products, identified by their visible-UV spectra, were *cis*- and *trans*-[(en)₂Co(NO₂)₂]⁺, *cis*- and *trans*-[(en)₂Co(OH₂)(NO₂)]²⁺, and a trace of *cis*-[(en)₂Co(NO₂)(C₂O₄)]. In contrast to the relatively facile formation of the *trans* oxalato-nitrito-*N* isomer, the *cis* isomer was formed only on prolonged heating. The principal side products were *cis*- and *trans*-[(en)₂Co(OH₂)(NO₂)]²⁺, *cis*-[(en)₂Co(NO₂)₂]⁺, and an uncharacterized orange, 1+ complex.

Both oxalato-nitrito isomers exhibit an intense charge-transfer band, ca. 240 nm, in common with other well-characterized (nitrito-*N*)cobalt(III) complexes.¹² The IR spectra of the *cis* and *trans* isomers exhibit intense absorption bands at 1615 and 1585 cm⁻¹, respectively, which are not removed by deuteration of the amines, and at ca. 1300 and at 775 cm⁻¹, characteristic of the oxalato groups.^{5a,6} The corresponding bands for the bidentate oxalato ligand in [(en)₂Co(C₂O₄)]Cl occur at 1690, 1670, 1645, 1410, and 795 cm⁻¹. IR bands for bridged oxalato ligands have been reported⁶ at 1635 and 1302 cm⁻¹, but the charge-neutral character of the present complexes and their stoichiometry, [(en)₂Co(NO₂)(C₂O₄)], rule out such bridged structures. Bands characteristic of nitrito-*N* coordination¹³ are found at 1405 and 1420, at 1340 and 1325, and at 825 and 815 cm⁻¹ for the *cis* and *trans* isomers, respectively. Nitrito-*O* coordination is precluded by the absence of prominent bands at 1110–1050 cm⁻¹,¹³ not attributable to C–C stretching.

The ¹³C and ¹H NMR spectra of the complexes readily distinguish the isomeric forms. The *trans* isomer has a single strong peak in the ¹³C spectrum at 47.46 ppm for the methylene carbons and two weak resonances at 170.11 and 178.34 ppm for the monodentate oxalate; the ¹H spectrum in the CH₂ region consists of a broad symmetric singlet at 2.75 ppm. The

(7) Cooper, J. N.; McCoy, J. D.; Katz, M. G.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 2265.

(8) Salzberg, H. W.; Morrow, J. I.; Cohen, S. R.; Green, M. E. "Physical Chemistry Laboratory"; Macmillan: New York, 1978; p 475.

(9) G. G. Schlessinger, "Inorganic Laboratory Preparations"; Chemical Publishing Co.: New York, 1962; p 237.

(10) Werner, A. *Justus Liebigs Ann. Chem.* **1912**, *386*, 252.

(11) Asperger, S.; Ingold, C. K. *J. Chem. Soc.* **1956**, 2862.

(12) Yamasaki, K.; Hidaka, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2624.

(13) Reference 5a, pp 220–224.

Table I. Acid Dissociation Quotient for $[(en)_2Co(NO_2)(C_2O_4)H]^+$ Isomers^a

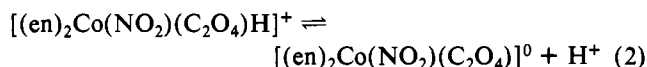
$10^2[H^+]/M$	$\epsilon_\lambda/M^{-1} \text{ cm}^{-1}$					$10^3K_A/M$
	10.0	4.44	2.22	1.11	0.001	
trans	1326	1380	1455	1554	1835	11.3 ± 0.3
cis	1288	1408	1599	1860	2829	8.0 ± 0.1

^a 25 °C; $\mu = 0.10$ (LiClO₄). Total complex concentrations: trans, 4.8×10^{-4} M; cis, 2.9×10^{-4} M. λ/nm : 330, trans; 300, cis.

cis isomer exhibits four resonances of roughly equal intensities in the ¹³C spectrum at 47.94, 47.57, 46.27, and 45.99 ppm; due to the low solubility of the cis complex, the expected weak doublet due to the monodentate oxalate could not be distinguished from noise after 34 000 pulses. In the ¹H spectrum the CH₂ region consists of an asymmetric pattern with principal peaks at 2.82, 2.73, 2.60, and 2.54 ppm. These data confirm the trans and cis identifications of the isomers and, for the trans oxalato-nitrito isomer, establish the nonequivalence of the carboxylate carbons and, thus, the monodentate character of the oxalato group. For comparison, NMR spectra of the bidentate oxalato complex salt, $[(en)_2Co(C_2O_4)]Cl$,¹⁴ were also obtained. The ¹³C spectrum consists of a doublet in the CH₂ region of 46.16 and 44.10 ppm and a weak singlet for the oxalate at 169.51 ppm; in the ¹H spectrum, a skewed singlet at 2.77 ppm in the CH₂ region was found.

Reactivity

Aquation. In solution at pH 5–6, the two isomers undergo slow decomposition, 16–25% in 9 days, yielding principally the aqua-nitrito-*N* species. Failure to observe nitrito aquation is consistent with the low aquation rates^{2,15} found for other (nitrito-*N*)bis(ethylenediamine)cobalt(III) complexes. At pH 1, in dilute HClO₄, both isomers bind to cation-exchange resins and elute with a mobility indicative of a 1+ species. The sorbed species are readily eluted and recovered with a dilute (0.05 M) acetic acid-sodium acetate buffer, pH 6, demonstrating the reversibility of the protonation equilibrium, eq 2.



(14) Dwyer, F. P.; Reid, I. K.; Garvan, F. L. *J. Am. Chem. Soc.* **1961**, *83*, 1285.

(15) Pethybridge, A. D.; Spiers, D. J. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 64.

pK_A 's were estimated at 25 °C for the two isomers by use of absorbances in the near-UV region^{16a} at pH 1, at pH 5, and with dilute HClO₄ of intermediate concentrations (Table I): trans, $10^3K_A = 11.3 \pm 0.3$, $pK_A = 1.95$; cis, $10^3K_A = 8.0 \pm 0.1$, $pK_A = 2.10$. These K_A 's are comparable to those reported for $[(NH_3)_5Co(C_2O_4)H]^{2+}$, 8.8×10^{-3} ^{16a} and 6.3×10^{-3} .^{16b} Protonation of the complexes provides added confirmation of the monodentate character of the oxalato ligand in each, and the similarity of the pK_A 's establishes, in the absence of observed ¹³C oxalato resonances, the monodentate oxalato ligand in the cis isomer.

In 0.111 M HClO₄, the trans isomer aquates slowly at room temperature, yielding principally *trans*- $[(en)_2Co(NO_2)(OH_2)]^{2+}$ with $t_{1/2}$ ca. 3 h. On the same time scale, the cis isomer is quite inert, undergoing negligible absorptivity change in the absence of light. Apparently in bis(ethylenediamine)cobalt(III) complexes, a nitrito-*N* group trans to ligands such as chloro¹¹ and, as shown here, aqua or hydrogen oxalato, exerts a mild labilizing effect. Kinetics were not further pursued. Both complexes exhibit modest photochemical reactivity at pH 1, comparable to that reported for other bis-(acidato)(amine)cobalt(III) complexes¹⁷ undergoing principally photoredox with some photoaquation. For *cis*- $[(en)_2Co(NO_2)(C_2O_4)]$ the results are unambiguous; 350-nm radiation completely photolyzed a pH 1 solution with an overall quantum yield of 2×10^{-3} mol/einstein. The principal Co-containing products, as determined by their visible-UV spectra, were Co²⁺(aq) and approximately 10% of the bidentate oxalato complex, $[(en)_2Co(C_2O_4)]^+$. For *trans*- $[(en)_2Co(NO_2)(C_2O_4)]$, interpretation of the photolysis results is complicated by the concomitant acidolysis; qualitatively, under comparable conditions, a solution containing the trans isomer was photolyzed twice as fast as one containing the cis, with production principally of Co²⁺ and about 5% *cis*- $[(en)_2Co(OH_2)_2]^{3+}$.

Acknowledgment. J.N.C. expresses appreciation to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. *trans*- $[(en)_2Co(NO_2)(C_2O_4)]$, 85709-97-3; *cis*- $[(en)_2Co(NO_2)(C_2O_4)]$, 85760-73-2; *trans*- $[(en)_2CoCl_2]Cl$, 14040-33-6; *cis*- $[(en)_2Co(Cl)(NO_2)]Cl$, 14221-34-2.

(16) (a) Andrade, C.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1087. (b) Ting, S.-F.; Kelm, H.; Harris, G. M. *Ibid.* **1966**, *5*, 696.

(17) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970; p 216.