which was insoluble in polar organic solvents and decomposed under vacuum.

The structural similarity of triNC to bidentate 1,3-diisocyanopropane which is known[3] to bridge Rh–Rh-bonded dimers $Rh_2(bridge)_4^{2+}$ suggested that triangular rhodium clusters could be formed with triNC. With the procedure used in the preparation of $Rh_2(bridge)_4^{2+}$, triNC was reacted with $[Rh(COD)Cl]_2$ in $CH_2Cl_2$ to yield a dark red precipitate which was insoluble in common organic solvents. The insolubility of this material like the other products obtained from reactions of triNC with metal clusters suggests that triNC probably forms polymeric products rather than simple clusters.

On the contrary, triNC reacts readily with mononuclear compounds. Besides the reaction with $Fe(CO)_5$ to give triNC$[Fe(CO)_4]_3$, reactions of triNC with $[M(CO)_5I][Et_4N]$ (M = Cr, W) and $Ag^+$ produce the corresponding triNC$[M(CO)_5]_3$ complexes (M = Cr (II); M = W (III)), which were fully characterized by their spectroscopic and analytical data. The complexes II and III are soluble in chlorinated hydrocarbon solvents, slightly soluble in aromatic hydrocarbons, and insoluble in saturated hydrocarbons. They are much more stable than complex I, and only a slight darkening was observed when they were exposed for several days to air and light. Their IR and $^1H$ and $^{13}C$ NMR spectra indicate that these complexes have a structure in which the isocyano groups are all-equatorial and one $M(CO)_5$ moiety is coordinated to each isocyanide donor. In their $^{13}C$ NMR spectra, two CO resonances with an intensity ratio of 1:4 are observed, which is consistent with CO groups trans and cis to the isocyanide ligand in an octahedral complex. Attempts to expel a CO group from each of the metal atoms in II or III by refluxing in heptane or by photolysis ($\lambda$ = 254 or 360 nm), thereby providing an opportunity for the formation of an $M_3$ metal–metal-bonded cluster, yielded only the starting complexes.

Despite the several favorable factors which suggest that triNC should be capable of coordinating to a triangle of metal–metal-bonded atoms, there is no evidence at this time that it does so. All complexes isolated at this point involve the coordination of mononuclear moieties to the isocyanide groups in the all-equatorial conformation (structure B) of triNC.

**Acknowledgment.** Support of this research by a grant (No. CHE78-07913) from the National Science Foundation is very much appreciated. The JEOL FX-90Q spectrometer was purchased with funds partially provided by the NSF. A loan of ruthenium trichloride from Matthey-Bishop, Inc., is greatly appreciated.

**Registry No.** I, 75045-78-2; II, 75030-47-6; III, 75045-79-3; triNC, 75045-77-1; trif, 75030-35-2; tach, 26150-46-9; $Fe(CO)_5$, 13463-40-6; $[Cr(CO)_5I][Et_4N]$, 14780-98-4; $[W(CO)_5I][Et_4N]$, 14781-01-2; acetic formic anhydride, 2258-42-6.

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# Preparation and Characterization of $[(en)_2Co(S_2O_3)]^+$, a Cobalt(III) Complex Containing Chelated *O*,*S*-Thiosulfate

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*Received March 26, 1980*

Early reports[1] of the preparation of $[(en)_2Co(S_2O_3)]^+$, in which the thiosulfate functions as an O,S-chelating ligand, appear to have been in error.[2] In the course of attempting to prepare crystalline salts of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$,[3] we have isolated what we believe to be authentic $[(en)_2Co(S_2O_3)]^+$ as both the perchlorate and the iodide salts.

**Table I.** IR Spectral Parameters for Salts of $[(en)_2Co(S_2O_3)]^{+\ a}$

| anion | $\nu$, $cm^{-1}$ (intensity) |
|---|---|
| $ClO_4^-$ | 3290 (vs), 3280 (vs, sh), 3250 (vs, sh), 3240 (vs), 3150 (s, sh), 3140 (s), 1590 (m), 1320 (w), 1280 (w), 1230 (s), 1200 (m), 1170 (w, sh), 1130–1110 (vs, br), 1090–1060 (vs, br), 1045 (s), 1000 (m), 930 (m), 890 (vw), 880 (vw), 780 (vw), 760 (vw), 660 (s), 620 (m), 615 (m), 610 (m), 580 (w), 535 (m) |
| $I^-$ | 3240 (vs), 3190 (vs), 3100 (vs), 1580 (m), 1320 (w), 1270 (w), 1230 (s), 1205 (m, sh), 1120–1110 (vs, br), 1090 (m, sh), 1050 (s), 1000 (s), 925 (m), 890 (w), 875 (vw), 790 (vw), 765 (vw), 655 (s), 580 (w), 545 (m) |

[a] In Nujol mulls; v = very, s = strong, m = medium, w = weak, br = broad, sh = shoulder.

## Experimental Section

**General Data.** All common laboratory chemicals were of reagent grade. Ion-exchange materials and procedures were as previously specified.[3] Visible–UV spectra (aqueous solutions, 200–700 nm) and spectrophotometric kinetic data were obtained with a Beckman DBGT instrument equipped with a thermostated cell housing. IR spectra in KBr wafers or Nujol mulls were obtained by use of a Perkin-Elmer 337 instrument with KBr optics. Conductances were measured with an Industrial Instruments conductivity bridge using Pt-black electrodes in a cell calibrated against KCl solutions. Elemental analyses were conducted by Galbraith Laboratories, Knoxville, Tenn.

**(Thiosulfato-*O*,*S*)bis(ethylenediamine)cobalt(III) Salts ($[(en)_2Co(S_2O_3)]X$, X = $ClO_4^-$, $I^-$).** The complex *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$, containing S-bonded monodentate thiosulfate, was prepared as previously described[3] and purified by cation-exchange chromatography on Sephadex SP-C25 in the $Li^+$ form. As previously noted,[3] upon elution with 0.25 M $LiClO_4$ the leading edge of the brown band containing *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ was distinctly red. The brown eluate was flash evaporated (temperature maintained at <20 °C) to near dryness, and this solution was further dehydrated by successive additions of absolute methanol or ethanol followed by repeated flash evaporation. On standing, this concentrated solution yielded a dark red solid, the supernatant being faintly brown. The red solid was triturated with an equal volume of 0 °C water to remove coprecipitated $LiClO_4$, separated by filtration, washed with absolute methanol, and then dried in air. Anal. Calcd for $[(en)_2Co(S_2O_3)]ClO_4$: C, 12.3; N, 14.3; H, 4.10; Co, 15.1; S, 16.4; Cl, 9.09. Found: C, 12.8; N, 14.4; H, 4.20; Co 15.3; S, 16.6; Cl, 9.25. The solubility of the perchlorate salt in 0 °C water is ca. 30 mg/mL. The less soluble iodide salt is prepared by adding excess solid NaI to a freshly saturated (room-temperature) solution of the perchlorate salt and then rapidly cooling the solution to 0 °C. IR spectra parameters for both salts are given in Table I. Visible–UV parameters (freshly dissolved solid; $\lambda_{max}$ ($\epsilon$) in nm and $M^{-1}$ $cm^{-1}$ are 530 (144), 276 (12 100), and 206 (12 000) for the perchlorate salt and 530 (146), 278 (11 800), and 223 (22 100) for the iodide salt.

## Results

The red $[(en)_2Co(S_2O_3)]^+$ cation is displaced from the Sephadex SP-C25 cation-exchange matrix by 0.25 M $LiClO_4$ somewhat more readily than is the original brown *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ cation; the spectrum of the product resulting from aquation of the $[(en)_2Co(S_2O_3)]^+$ coincides quantitatively with that of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$,[3] and no other products are detected (eq 1).

$$\textit{trans-}[(en)_2Co(OH_2)(S_2O_3)]^+ \xrightleftharpoons[H_2O]{\text{dehydration}} [(en)_2Co(S_2O_3)]^+ \qquad (1)$$

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0020-1669/80/1319-3856$01.00/0

The kinetics of the conversion of $[(en)_2Co(S_2O_3)]^+$ to *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ in 0.10 M $LiClO_4$ (monitored at 530 nm) are well described by the first-order-rate expression (2), where the

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obsd}t) \tag{2}$$

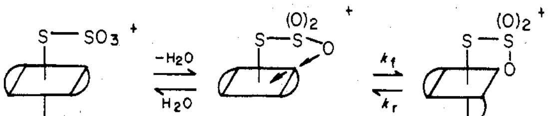
subscripts denote the time of that absorbance reading. The observed first-order rate parameters, $k_{obsd}$, are independent of $[H^+]$ over the pH range 2–6 and of the initial cobalt concentration over the range 0.005–0.010 M. The temperature dependence on the rate parameters ($10^3k_{obsd}$ ($T$) in $s^{-1}$ and °C: 0.067 ± 0.003 (15.0), 0.275 ± 0.014 (25.2), 1.07 ± 0.04 (35.3), 2.82 ± 0.19 (45.0)) yields apparent activation parameters $\Delta H^* = 22.3 \pm 0.8$ kcal/mol and $\Delta S^* = 0.0 \pm 2.4$ eu ($\mu = 0.10$ M).

For $[(en)_2Co(S_2O_3)]ClO_4$, the charge per cobalt is determined to be 0.97 ± 0.05 by adsorbing a weighed amount of the complex on Dowex 50-X8 cation-exchange resin in the acid form and then determining the acid released by NaOH titration. For $[(en)_2Co(S_2O_3)]I$, the I:Co ratio is determined to be 1.0 ± 0.1 by adsorbing a weighed amount of the complex on Sephadex SP-C25 cation-exchange matrix and then spectrophotometrically determining the amount of iodide in the eluant ($\epsilon(I^-) = 13\,000$ $M^{-1}$ $cm^{-1}$ at 225 nm). The aqueous conductance per mole of cobalt at 25 °C, 0.01 M solution of $[(en)_2Co(S_2O_3)]ClO_4$, is 92 ± 1 mho $cm^2$/mol, and this value does not vary significantly during conversion to *trans*-$[(en_2Co(OH_2)(S_2O_3)]^+$. For comparison, the conductance of $[(en)_2Co(CO_3)]ClO_4$ under equivalent conditions is 86 ± 1 mho $cm^2$/mol.

## Discussion

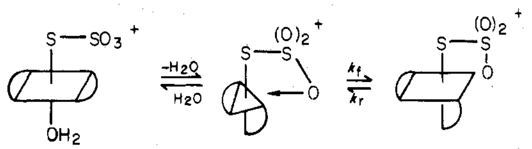
The conclusions that $[(en)_2Co(S_2O_3)]^+$ contains chelated *O,S*-thiosulfate and is not a perchlorato complex or a thiosulfato-bridged polymer are based on the following direct and indirect evidence. (1) The mode of preparation and elemental analysis of $[(en)_2Co(S_2O_3)]ClO_4$ establish that the $S_2O_3$:$(en)_2Co$:$ClO_4$ ratio is 1:1:1. (2) The existence of an intense absorption maximum at 276 nm establishes the presence of a Co–S bond since this ligand-to-metal charge-transfer band characteristically arises whenever sulfur is coordinated to cobalt(III).[3,4] (3) The intensity of the d–d transition of $[(en)_2Co(S_2O_3)]^+$ is more than twice that of *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ ($\epsilon_{530} = 146$ and 65 $M^{-1}$ $cm^{-1}$, respectively), and it is well established that because of lower symmetry cis complexes have more intense d–d transitions than do trans complexes.[5] (4) Since the iodide salt has the same visible–UV spectrum as does the perchlorate salt, neither the iodide nor the perchlorate are coordinated to the cobalt center. In addition, the IR spectrum of the perchlorate salt indicates the presence of ionic $ClO_4^-$ rather than coordinated $ClO_4^-$ (Table I). (5) The observations of unit charge per cobalt, unit cobalt-to-iodide ratio for the iodide salt, aqueous conductivity equivalent to that of a known one-to-one electrolyte, and ion-exchange elution characteristics very similar to those observed for *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ establish that $[(en)_2Co(S_2O_3)]^+$ is a monomeric complex of 1+ formal charge. (6) Both the iodide and perchlorate salts exhibit a medium-strength IR band at 925–930 $cm^{-1}$ which does not arise from free perchlorate, the bis(ethylenediamine)cobalt(III) moiety, or monodentate thiosulfate; this band may arise from the chelated *O,S*-thiosulfate ligand, corresponding to the 971-$cm^{-1}$ band reported for *O,S*-thiosulfate in $Ni(tu)_4(S_2O_3)\cdot H_2O$ (tu = thiourea).[6] Thus, the formulation of $[(en)_2Co(S_2O_3)]^+$ as containing *O,S*-thiosulfate results largely from the fact that there is no other chemically reasonable formulation that will account for all the experimental observations. Efforts to obtain single crystals of $[(en)_2Co(S_2O_3)]ClO_4$ are under way in order to verify positively this formulation through X-ray analysis.

Given that $[(en_2Co(S_2O_3)]^+$ contains chelated *O,S*-thiosulfate, the interconversion of this complex with *trans*-$[(en_2Co(OH_2)(S_2O_3)]^+$ (eq 1) represents a remarkably facile cobalt(III) cis–trans transformaton. Trans-substituted bis(ethylenediamine)cobalt(III) complexes often aquate with stereochemical change,[7] and examples are now known of cis complexes which also undergo isomerization during substitution reactions.[8] Tobe[9] and others[7,8] have noted that the factors which control the extent of cis–trans interconversion during substitution reactions on bis(ethylenediamine)cobalt(III) centers are both varied and subtle. The predominant factors contributing to the efficient interconversion between *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ and $[(en)_2Co(S_2O_3)]^+$ are presumably the established[3] trans-labilizing ability of S-bonded thiosulfate and the inherent ability of thiosulfate to form a chelate ring. By acceptance of the well-established dissociative mode of activation for cobalt(III) substitution reactions,[7–9] these effects can be readily visualized within a scheme (eq 3) based upon



(3)

a square-pyramidal intermediate which results from labilized loss of the water ligand situated trans to the coordinated sulfur atom. An equivalent scheme (eq 4) can be based upon a



(4)

trigonal-bipyramidal intermediate. In both schemes the five-coordinate intermediate is converted to a six-coordinate complex through either attack by water to yield *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ or attack by a pendant oxygen atom of the S-bonded thiosulfate ligand to yield $[(en)_2Co(S_2O_3)]^+$. The microscopic reverse of attack by the pendant oxygen atom ($k_f$) is *unimolecular* Co–O bond fission ($k_r$), a mode of activation which is in harmony with the observed pH independence of the rate of disappearance of $[(en)_2Co(S_2O_3)]^+$; if conversion of $[(en)_2Co(S_2O_3)]^+$ to *trans*-$[(en)_2Co(OH_2)(S_2O_3)]^+$ involved *bimolecular* attack by water, the observed rate would be expected to be strongly pH dependent. For an equilibration such as we propose $k_{obsd} = k_f' + k_r'$; given the apparent completeness of the aquation, we assume $k_r' \gg k_f'$. The rate of disappearance of $[(en)_2Co(S_2O_3)]^+$ is about a factor of 10 faster than the rate at which *cis*- and *trans*-$[(en)_2Co(OH_2)(OOCCH_3)]^{2+}$ come to equilibrium,[10] a reaction which also involves Co–O bond fission in the rate-determining step. The greater lability of the thiosulfate system presumably reflects the lower formal charge on the complex as well as the stability of the five-coordinate intermediate containing sulfur; the latter is a natural consequence of the trans-labilizing ability of S-bonded thiosulfate.[3] Studies designed to probe further the chemistry of thiosulfate when S-bonded to cobalt(III) are currently in progress.

**Acknowledgment.** Financial support by the National Science Foundation, Grant No. CHE76-19681 (E.A.D.), the NSF

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Program for Support of Small College Faculty (E.A.D. and J.N.C.), and the donors of the Petroleum Research Fund (J.N.C.), administered by the American Chemical Society, is gratefully acknowledged.

**Registry No.** $[(en)_2Co(S_2O_3)]ClO_4$, 74911-63-0.

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## Photochemistry of Cobalt Carbonyl Complexes Having a Cobalt–Silicon Bond and Its Importance in Activation of Catalysis

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*Received July 8, 1980*

We wish to report results of experiments that establish the relative importance of photochemical cleavage of the Co–Si bond vs. the dissociative loss of CO in $R_3SiCo(CO)_4$ (eq 1 vs. eq 2). We recently showed[1] that photogeneration of 17-valence-electron, Co-centered radicals can lead to catalysis of alkene isomerization, hydrosilation, and hydrogenation. Reaction of $R_3SiCo(CO)_4$ according to eq 1 is of interest in that the 17-valence-electron radical $\cdot Co(CO)_4$ could effect the same alkene/$HSiR_3$ reactions known[2] to be catalyzed by $Co_2(CO)_8$. It is believed that $R_3SiCo(CO)_4$ represents the ultimate fate of Co in the $Co_2(CO)_8$ catalyzed hydrosilation reaction and that it is not an active thermal catalyst at the temperatures that can be used for $Co_2(CO)_8$.[2] We thus wondered whether the $Co_2(CO)_8$ catalyst could be regenerated from irradiation of $R_3SiCo(CO)_4$ according to eq 1 and 3.

$$R_3SiCo(CO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} R_3Si\cdot + \cdot Co(CO)_4 \qquad (1)$$

$$R_3SiCo(CO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} R_3SiCo(CO)_3 + CO \qquad (2)$$

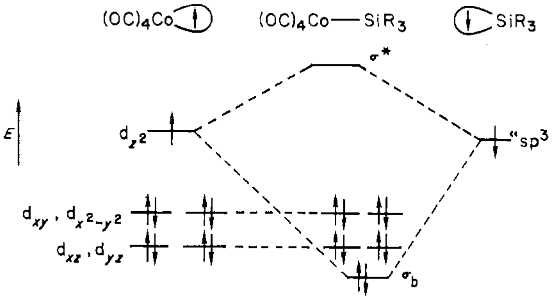
$$2\cdot Co(CO)_4 \rightarrow Co_2(CO)_8 \qquad (3)$$

The relative importance of the two photoreactions represented by eq 1 and 2 is of fundamental interest, since there is considerable ambiguity concerning the importance of primary photogeneration of 17-valence-electron vs. 16-valence-electron fragments from coordinatively saturated, 18-valence-electron species having both 2- and 1-electron donor ligands.[3] For $R_3SiCo(CO)_4$ the orbital diagram in Scheme I is appropriate,[4] and it is apparent that all lowest excited states involve population of $\sigma^*(d_{z^2})$ resulting in weakening of the $\sigma$ bonding between Co and all of the five ligands.

### Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 180 grating spectrophotometer in matched 1.0-mm or 0.1-mm path length amalgam-sealed NaCl cells. Low-temperature spectra were taken by using a Cyrogenics Technology, Inc., Spectrim II cryocooler in conjunction with the spectrophotometer; a 1.1-mm path length uncompensated $CaF_2$ cell was constructed to interface with the cold head. Electronic spectra were taken on a Varian Associates Cary Model 17 UV–vis–near–IR spectrophotometer, in 1.0-cm quartz or 1.1-cm Pyrex cells. Gas–liquid chromatography was performed on a Varian Associates Model 1440 or 2440 gas chromatograph equipped with flame ionization detectors and interfaced with either a Hewlett-Packard Model 3370S electronic recording integrator or a Varian Model A25 strip chart recorder. Hydrocarbon analyses (against internal standard hexane) were carried out on columns of 20% propylene carbonate on Chromosorb P (Johns-Manville, 30 ft × $^1/_8$ in., 20 °C). Hydrosilation products were analyzed (against internal standard decane) on columns of 20% $\beta,\beta'$-oxydipropionitrile on Gaschrom Q (Applied Science Laboratories, 30 ft × $^1/_8$ in., 60 °C). Organic products of the photolyses of $Ph_3SiCo(CO)_4$ in pentene or isooctane were separated on columns of 1.5% OV-101 on Chromosorb P ($^1/_8$ in. × 5 ft, 120–250 °C, programmed at 10–20 °C/min). Nuclear magnetic resonance spectra were obtained with a Hitachi Perkin-Elmer R-24B or Varian T-60 spectrometer ($^1$H, 60 MHz) or with a Jeolco FX-90Q spectrometer ($^1$H, 90 MHz). Mass spectra were obtained on a Varian MAT 44 spectrometer, interfaced with a Varian Series 1400 gas chromatograph for GC/MS.

Scheme I. One-Electron Orbital Diagram for $R_3SiCo(CO)_4$



All air-sensitive organometallic compounds were handled under an argon atmosphere by conventional Schlenk techniques or under an atmosphere of prepurified nitrogen in a Vacuum Atmospheres Dri-Lab glovebox. Photosensitive solutions were handled under red safelights or in the dark. $Co_2(CO)_8$ (ROC/RIC, Strem) and $P(OPh)_3$ (Strem) were used as received. $PPh_3$ (Aldrich) and $HSiPh_3$ (Petrarch) were recrystallized from ethanol and pentane, respectively, before use. Alkenes (99%, PCR or Phillips Chemical Co.) were passed through activated alumina (MC&B chromatographic grade, 80–325 mesh) prior to use and stored in amber bottles at 4 °C. Triethylsilane (Petrarch) was treated similarly. $Co_4(CO)_{12}$ was prepared by heating $Co_2(CO)_8$ under $N_2$ in isooctane at 80–90 °C for 12 h, filtering off the product, and recrystallizing it from benzene/isooctane under $N_2$. $R_3SiCo(CO)_4$ (R = Et, Ph) were prepared by the literature method of Chalk and Harrod.[5] Solvents were reagent grade or better; isooctane was spectrophotometric grade. For work with air- or water-sensitive species, solvents were distilled under argon from appropriate drying agents.

Solutions for irradiation were hermetically sealed into 13-mm o.d. Pyrex ampules after at least four freeze-pump-thaw degassing cycles under high vacuum. Alternatively, the organometallic was added in the glovebox to previously degassed solvent, and the mixture was transferred to o.d. Pyrex tubes with ground glass joint tops which were then sealed with rubber septa. o.d. Pyrex Irradiation samples were generally 1–4 mL in volume, $\sim 10^{-3}$ M in metal carbonyl for catalysis, and $10^{-2}$–$10^{-4}$ M for spectral studies. Light intensities were determined by ferrioxalate actinometry.[6] Near-ultraviolet irradiation was generated by two General Electric Blacklites ($\lambda_{max}$ = 355 ± 20 nm, $I \approx 2 \times 10^{-6}$ einstein/min) or a high-pressure mercury arc lamp (Bausch and Lomb, Model SP200, 200 W) with an 18-cm water filter to remove infrared radiation. Monochromatic light was supplied by medium-pressure mercury arc lamps (Hanovia, 450 or 550 W) filtered with Corning glass filters to isolate the desired emission ($I \approx 10^{-7}$ ein-

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