brown solids. The IR spectra of I show two strong ν(CO) stretching frequencies in the range 1900–2000 cm^{-1} and two ν(NN) bands of medium to strong intensity between 1550 and 1615 cm^{-1} which are probably coupled with the vibrational modes of the attached phenyl groups.[10] Proton NMR spectra show the expected cyclopentadienyl and ligand signals.

The compounds I are similar in chemical behavior to the mononuclear analogues $CpMo(N_2Ar)(CO)_2$.[8] They react with PPh_3 in boiling methylcyclohexane to afford the corresponding orange substituted products $DiN_2[CpMo(PPh_3)(CO)]_2$ (IIa) and t-$BuDiN_2[CpMo(PPh_3)(CO)]_2$ (IIb) whose IR spectra show only one ν(CO) absorption at ~1865 cm^{-1} and one strong ν(NN) vibration around 1510 cm^{-1}. Compounds IIa and IIb rapidly react with monodentate diazonium ligands such as $[p\text{-}CH_3C_6H_4N_2][BF_4]$ in acetone at −78 °C to give the corresponding purple bis(aryldiazenato) complexes $DiN_2[CpMo(N_2C_6H_4CH_3\text{-}p)(PPh_3)]_2(BF_4)_2$ (IIIa) and t-$BuDiN_2[CpMo(N_2C_6H_4CH_3\text{-}p)(PPh_3)]_2(BF_4)_2$ (IIIb), which show no ν(CO) absorptions in their IR spectra but exhibit four bands between 1550 and 1655 cm^{-1} in the ν(NN) region. In their proton NMR spectra, the methyl group signals of the *p*-tolyl ligands of IIIa and IIIb and the *tert*-butyl group signals of IIIb appear as two lines with intensity ratios of approximately 60:40. This observation may be tentatively explained by considering the chiral centers at the two molybdenum atoms, giving rise to a mixture of meso and *d,l* diastereomers. These two diastereomers would account for the NMR observations.

The complexes III could also be obtained by reactions of $CpMo(N_2C_6H_4CH_3\text{-}p)(PPh_3)(CO)$ with DiN_2^{2+} or t-$BuDiN_2^{2+}$ in acetone at −78 °C. Such reactions, however, did not provide any evidence for the formation of chelated complexes of the type $[CpMo(DiN_2 \text{ or } t\text{-}BuDiN_2)(PPh_3)]^+$ resulting from the displacement of the carbonyl and *p*-tolyldiazonium groups. The metathesis reaction between the t-$BuDiN_2^{2+}$ ligand and the coordinated *p*-tolyldiazonium groups in the complex $[CpMo(N_2C_6H_4CH_3\text{-}p)_2(PPh_3)]^{+}$[4e] also did not take place even after several days' stirring in acetone at room temperature.

In an attempt to explore further the possibility of preparing chelate complexes of DiN_2^{2+}, other metal carbonyl anions were reacted with this ligand. The reactions of $Mn(PPh_3)_2(CO)_3^-$, $Mn(CO)_5^-$, and $Co(CO)_4^-$ with DiN_2^{2+} at low temperature (−78 °C) gave deeply colored solutions; however, no characterizable products containing the N_2 moiety could be isolated after warming of the reaction mixtures to room temperature. Only in the case of the reaction between $Co(CO)_4^-$ and DiN_2^{2+} at −78 °C in the presence of triphenylphosphine was an unstable product having ν(CO) at 2000 (s) and 1955 (s, br) cm^{-1} and ν(NN) at 1693 (m) and 1645 (sh) cm^{-1} in dichloromethane solution observed. The similarity of its IR data and chemical behavior to that of $Co(N_2Ph)(PPh_3)(CO)_2$[11] suggests that this compound is of the type $DiN_2[Co(PPh_3)(CO)_2]_2$ in which the organic aryldiazenato ligand bridges the two Co atoms.

Reactions of the potentially chelating bidentate aryldiazenato ligands with the anionic metal complexes investigated so far seem to indicate that, unlike the related isocyanide and nitrile ligands, these prefer to bridge two metal centers rather than chelate to one. This may be due to the less favorable geometry resulting from a bent N–N–Ar geometry or other factors.

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Registry No. Ia, 75045-81-7; Ib, 75030-72-7; Ic, 75030-73-8; Id, 75030-74-9; IIa, 75030-75-0; IIb, 75030-76-1; IIIa, 75030-78-3; IIIb, 75045-83-9; $DiN_2^{2+}(BF_4^-)_2$, 75030-56-7; t-$BuDiN_2^{2+}(BF_4^-)_2$, 75030-58-9; $CpMo(CO)_3^-$, 12126-18-0; $CpW(CO)_3^-$, 12126-17-9; $DiNH_2$, 52411-34-4; t-$BuDiNH_2$, 75030-59-0; $DiN_2[Co(PPh_3)(CO)_2]_2$, 75030-79-4; $Co(CO)_4^-$, 14971-27-8.

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Synthesis and Metal Carbonyl Complexes of *cis,cis*-1,3,5-Triisocyanocyclohexane, an Unusual Tridentate Ligand

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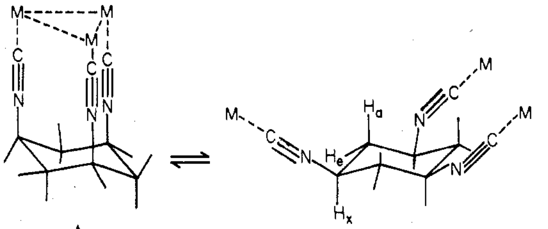
Relatively little is known about the coordination chemistry of multidentate isocyanide ligands as compared to their monodentate analogues.[2] The synthesis and reactions of a series of alkyl[3-5] and aryl[6] diisocyanide ligands were recently investigated. We wish to report herein the synthesis and chemical properties of an unusual tridentate triisocyanide ligand, *cis,cis*-1,3,5-triisocyanocyclohexane (triNC), which is potentially capable of coordinating to a triangular array of three metal–metal-bonded atoms. The ligand may assume either of two forms: A or B. In form A the NC groups are all axial and the three carbon atoms describe an equilateral triangle whose edge is about 2.5 Å. Molecular models indicate that this distance is comparable to metal–metal bond lengths in triangular arrays of metal atoms in many metal carbonyl clusters. Form A of triNC is related to the bidentate 1,3-diisocyanopropane (bridge) ligand which is known to bridge two interacting Rh atoms in the $Rh_2(bridge)_4^{2+}$ complexes.[3] These considerations suggested that triNC may be capable of coordinating to and perhaps stabilizing triangular arrays of metal atoms in simple M_3 clusters or in larger polyhedra with triangular faces.



A

B

triNC

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Table I. IR and ^1H and ^{13}C NMR Spectroscopic Data for the Compounds

compd	IR,[a] cm^{-1}			^1H NMR[b] (δ)				^{13}C NMR[b] (δ)			
	ν(CO)	ν(C≡N)	other[c]	H_a[d]	H_e[d]	H_x[d]	other	CO	NC	CH[e]	CH_2[f]
(triNC)[Fe(CO)$_4$]$_3$ (I)	2053 s 1992 s 1965 vs	2174 m		2.03 q	2.80 d[g]	3.85 tt		211.8 s	166.1 s	50.9 s	37.3 s
(triNC)[Cr(CO)$_5$]$_3$ (II)	2060 m 1994 w, sh 1955 vs, br	2153 m		2.03 q	2.83 d[g]	3.78 tt		215.6 s[h] 214.2 s[i]	169.3 s	49.6 s	38.2 s
(triNC)[W(CO)$_5$]$_3$[j] (III)	2061 m 1991 w, sh 1949 vs, br	2155 m		2.09 q	2.89 d[g]	3.89 tt		195.9 s[h] 194.3 s[i,k]	148.0 s	49.7 s	38.2 s
triNC		2145 s		1.88 q	2.64 dt	3.47 tt			158.6 s	46.5 s	37.8 s
trif[l]			3260 s[m] 1645 vs, br[p] 1548 s[q]	1.31 q[n]	2.15 dt[n]	3.94 tt[n]	7.99 s[o]				

[a] In CH_2Cl_2 solution unless otherwise stated; vs = very strong, m = medium, sh = shoulder, br = broad. [b] In $CDCl_3$ unless otherwise stated; s = singlet, d = doublet, dt = doublet of triplets, tt = triplet of triplets. For proton designation, see structure B. [c] Nujol mull. [d] The following coupling constants were observed for the complexes and triNC (see also text): $J_{gem} \simeq J_{ax} \simeq 12.0$ Hz; $J_{ex} \simeq 3.5$ Hz. [e] Methine carbons. [f] Methylene carbons. [g] Only $J_{gem} \simeq 12.0$ Hz is observed owing to the broadness of the bands. [h] Trans CO. [i] Cis CO. [j] ^{13}C NMR in CD_2Cl_2. [k] $J(^{183}W\text{–cis CO}) = 125$ Hz. [l] ^1H NMR in D_2O. [m] ν(NH). [n] Coupling constants: $J_{gem} \simeq J_{ax} \simeq 14.5$ Hz; $J_{ex} \simeq 4.5$ Hz. [o] δ(NHC*H*O); the signal due to the NH proton is not seen in D_2O due to H/D exchange. [p] ν(C≡O). [q] NH bending mode.

In the second form B of triNC, the NC groups are all equatorial. Steric factors would suggest that this is expected to be the more stable form of the free ligand. Should metals coordinate to the isocyanide groups in this form, separate mononuclear metal groups would bind to each NC donor.

A growing number of metal clusters[7] containing one or more monodentate isocyanide ligands supports the possibility that triNC in form A would coordinate to a triangular face of metals in such clusters. However, it has also been observed that the introduction of too many isocyanide ligands into these clusters will cause fragmentation to mononuclear complexes. The purpose of this investigation was to explore the possibility of stabilizing triangular arrays of metal atoms with triNC.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was distilled under N_2 from BaO; tetrahydrofuran (THF), benzene, toluene, diethyl ether, and heptane were distilled under N_2 from sodium. All other solvents were of reagent grade purity and were dried over molecular sieves without further purification. IR spectra were obtained with a Perkin-Elmer 281 spectrophotometer. Proton NMR spectra were recorded on a JEOL FX-90Q Fourier transform NMR spectrometer using tetramethylsilane (Me_4Si) as an internal standard in $CDCl_3$ solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DDS) as an internal standard in D_2O solutions. The proton-decoupled carbon-13 NMR spectra were run with the above instrument using the solvent as the standard, but all ^{13}C chemical shifts are reported in ppm downfield from Me_4Si. Tris(acetylacetonato)chromium(III) (~0.1 M) was added to the ^{13}C NMR solutions to reduce data collection time. Melting points were taken on a Thomas hot-plate apparatus and are uncorrected.

Starting Materials. The complexes $Fe_3(CO)_{12}$,[8] $Ru_3(CO)_{12}$,[9] $[M(CO)_5I][Et_4N]$[10] (M = Cr, W), and $[Rh(COD)Cl]_2$[11] (COD = 1,5-cyclooctadiene) were prepared according to literature methods. The compounds $Os_3(CO)_{12}$ and $Fe(CO)_5$ were purchased from Strem Chemicals and used without further purification. Dicobalt octacarbonyl (Strem Chem.) was freshly sublimed before use. *cis,cis*-1,3,5-Triaminocyclohexane (tach) which was used in the following preparations of triNC was prepared according to a literature procedure.[12]

Preparation of *cis,cis*-1,3,5-Triformamidocyclohexane (trif). To a vigorously stirred solution of tach (4.00 g, 31.0 mmol) in 400 mL of THF was added acetic formic anhydride[13] (8.5 mL, 8.5 g, 97 mmol) in one portion at room temperature. A white solid immediately precipitated from the solution. The reaction mixture was stirred for an additional 6 h; then it was poured into hexane (400 mL) and filtered. The crude product was dissolved in boiling absolute EtOH (300 mL). On slow cooling of the solution to room temperature, white needles which separated from solution were filtered and dried under vacuum to give a first crop of trif (2.8 g). Diethyl ether (100 mL) was added to the mother liquor, and the mixture was cooled to −20 °C overnight. The resulting white precipitate was then filtered and dried under vacuum, giving a second crop of trif (1.5 g). The total yield was 4.3 g or 65% (mp 265–267 °C). Anal. Calcd for $C_{12}H_{15}N_3O_3$: C, 50.69; H, 7.09; N, 19.70. Found: C, 50.68; H, 7.09; N, 7.09; N, 19.35. IR and ^1H NMR data for this compound as well as for triNC are listed in Table I.

***cis,cis*-1,3,5-Triisocyanocyclohexane (triNC).** A three-neck round-bottom flask equipped with a mechanical stirrer, dropping funnel, and inlet-outlet for N_2 was charged with trif (4.30 g, 20.2 mmol), and freshly distilled DMF (250 mL) was added at room temperature. The vigorously stirred solution of trif was then cooled to −50 to −55 °C by using a dry ice–acetone bath, and a solution of $SOCl_2$ (7.50 g, 63.0 mmol) in 40 mL of DMF was added dropwise over a period of ~30 min at such a rate that the temperature never exceeded −50 °C. After the addition was complete, the reaction mixture was warmed to −45 °C, and anhydrous Na_2CO_3 (25.0 g, 235 mmol) was added in one portion. The dry ice–acetone bath was removed and the reaction mixture allowed to come to room temperature; it was stirred for an additional 10–16 h. The colorless solution was then poured into 500 mL of ice water and extracted with C_6H_6 (2 × 300 mL). The benzene layer was subsequently extracted with H_2O (3 × 100 mL) and then dried over anhydrous Na_2SO_4. After filtration, evaporation to dryness gave a pale yellow oil which, on addition of 20 mL of hexane, gave the product as a white solid. The crude product may be sublimed (80 °C, 2×10^{-2} torr) onto a probe cooled with running water with only a slight decrease in yield (1.8 g, 56%) (mp 128–130 °C). Anal. Calcd for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.63; H, 5.61; N, 26.45. The mass spectrum of this compound gave a parent-ion peak at the expected *m/e* value of 159.

Preparation of Complexes. (triNC)[Fe(CO)$_4$]$_3$ (I). To a solution of triNC (0.318 g, 2.00 mmol) in 12 mL of toluene, previously degassed by freeze–pump–thaw cycles (3 times), cooled to −78 °C, was added $Fe(CO)_5$ (1.18 g, 6.02 mmol) in one portion. The system was

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evacuated at low temperature and then, after being warmed to room temperature, was heated at 70 °C. Every hour the reaction mixture was cooled to −78 °C, and the system was evacuated and reheated as above. After ~6 h the mixture turned brown. An IR spectrum showed that all of the triNC had reacted. The solution was taken to dryness under vacuum to give a sticky brown product. It was dissolved in degassed CH_2Cl_2 (50 mL), and the solution was filtered and treated with degassed heptane (30 mL). A white solid and a pale yellow solution were obtained. After filtration, a pale yellow crystalline compound began to precipitate from the solution to give the title compound (0.32 g, 24% yield). The complex is light and air sensitive, turning orange after a few hours' exposure (mp > 80 °C (progressively darkens without melting)). Anal. Calcd for $C_{21}H_9N_3O_{12}Fe_3$: C, 38.05; H, 1.37; N, 6.34. Found: C, 37.93; H, 1.99; N, 6.38. IR and ^1H and ^{13}C NMR data for this and the other complexes are listed in Table I.

(triNC)[Cr(CO)$_5$]$_3$ (II). A solution of $AgBF_4$ (0.74 g, 3.81 mmol) in 8 mL of acetone was added dropwise over a period of 20 min to a cold (0 °C) acetone solution (20 mL) of $[Cr(CO)_5I][Et_4N]$ (1.68 g, 3.75 mmol). After the addition was complete, the mixture was stirred a few minutes more and then filtered. To the orange filtrate, kept at 0 °C, was added a solution of triNC (0.20 g, 1.25 mmol) in 20 mL of acetone dropwise over a period of 5 min. After being stirred for an additional 20 min, the yellow-orange solution was allowed to come to room temperature and evaporated to dryness under a fast stream of N_2. Pentane/acetone (6:1 mixture, 40 mL) was added, and the yellow solution was filtered and again evaporated under N_2. The residue was dissolved in a minimum amount of CH_2Cl_2, and 20 mL of pentane was added slowly to form a layer. On cooling of the solution to −20 °C overnight, white crystals of the product precipitated. They were filtered and dried under vacuum to give a yield of 0.57 g (62%). (mp >125 °C (progressively darkens without melting)). Anal. Calcd for $C_{24}H_9N_3O_{15}Cr_3$: C, 39.42; H, 1.23; N, 5.71. Found: C, 39.42; H, 1.48; N, 5.75.

(triNC)[W(CO)$_5$]$_3$ (III). This compound was prepared by a procedure similar to that used for the Cr complex starting from $AgBF_4$ (0.74 g, 3.81 mmol), $[W(CO)_5I][Et_4N]$ (2.10 g, 3.75 mmol), and triNC (0.20 g, 1.25 mmol). After extraction with pentane/acetone, the yellow filtrate was taken to dryness, dissolved in 60 mL of Et_2O, and filtered, and the solution was taken to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2; a layer of pentane was added. Cooling overnight at −20 °C gave pale yellow crystals which were filtered and dried under vacuum (yield 0.92 g or 64%) (mp 165–167 °C dec). Anal. Calcd for $C_{24}H_9N_3O_{15}W_3$: C, 25.49; H, 0.80; N, 3.72. Found: C, 25.60; H, 1.09; N, 3.73.

Results and Discussion

The formylation of *cis,cis*-1,3,5-triaminocyclohexane (tach) and subsequent dehydration of the resulting triformamide with $SOCl_2/DMF$[14] gave in 36% overall yield the *cis,cis*-1,3,5-triisocyanocyclohexane (triNC) ligand. Other methods[15,16] of converting the triformamide to the triNC ligand gave yields of only 5–10%. The triNC ligand is a white solid soluble in chlorinated solvents, aromatic hydrocarbons, and diethyl ether but less soluble in saturated hydrocarbons. The ligand displays only one strong $\nu(C{\equiv}N)$ absorption at 2145 cm^{-1} in dichloromethane solution. Its ^1H NMR spectrum shows a quartet for the axial methylene H_a protons (see structure **B**) at δ 1.88 due to the near equivalence of the one geminal and two axial coupling constants ($J_{gem} \simeq J_{ax} \simeq 12.0$ Hz). The equatorial H_e protons appear as a doublet of triplets due to coupling with one geminal and two axial protons ($J_{ex} \simeq 3.5$ Hz), while the H_x protons appear as a triplet of triplets caused by coupling with two axial protons ($J_{ax} \simeq 12.0$ Hz) and two equatorial protons ($J_{ex} \simeq 3.5$ Hz). Such a pattern is similar to those observed for several cis,cis-1,3,5-trisubstituted cyclohexane compounds where the substituent groups are OH,[17] NH_3^+,[18] Cl,[19] OSO_2Ph,[12] or N_3.[12] On the basis of their ^1H NMR spectra, all were assigned the all-cis,all-equatorial conformation. These results suggest that triNC also has the all-cis,all-equatorial structure, i.e, form **B**.

Although the three isocyanide groups are equatorial in the free ligand, it was hoped that isomerization to the all-axial conformation (structure A) and coordination to a triangular cluster of metal atoms would occur. A related isomerization has been observed[18,20] when all-cis,all-equatorial 1,3,5-triaminocyclohexane reacts with metal ions to form complexes in which the three amino groups coordinate facially to the metal. A favorable series of triangular clusters for testing the ability of triNC to isomerize and coordinate to the three metal atoms is the $M_3(CO)_{12}$ group, where M = Fe, Ru, or Os. Their reactions with triNC might be expected to yield the $M_3(CO)_9$(triNC) clusters.

Reactions of the polynuclear metal carbonyls $M_3(CO)_{12}$ with monodentate RNC ligands, where R is usually an alkyl group, have been shown to give substituted products of the type $M_3(CO)_{12-n}(RNC)_n$ (n = 1–3).[7b,d] Fragmentation of these mixed carbonyl–isocyanide complexes has been observed for M = Fe ($n > 2$, R = Me; $n > 3$, R = *t*-Bu)[7b] and for M = Ru ($n > 3$).[7d] When equimolar triNC is added to a dilute solution of $Fe_3(CO)_{12}$ in THF at room temperature, a rapid reaction takes place. Chromatography of the reaction mixture on neutral alumina eluting with 1:1 THF/hexane gave a pale green band which showed $\nu(C{\equiv}N)$ and $\nu(CO)$ absorptions characteristic of $(RNC)Fe(CO)_4$ complexes,[21,22] in which the RNC ligand occupies an axial position in the trigonal-bipyramidal structure. An identical spectrum was obtained from the crude product of the reaction in toluene between triNC and $Fe(CO)_5$ in a 1:3 ratio under conditions similar to those reported in the literature for the reaction of $Fe(CO)_5$ with *p*-anisyl isocyanide.[21] In our case, it was possible to separate, by crystallization, one of the products which, on the basis of spectroscopic and analytical results, has been formulated as (triNC)[Fe(CO)$_4$]$_3$ (I), in which the ligand has the all-equatorial conformation and a $Fe(CO)_4$ group is coordinated to each isocyanide donor.

The ^{13}C NMR spectrum of I shows only one signal for the carbonyls at δ 212, indicating rapid exchange of the axial and equatorial CO groups. The mass spectrum (electron and chemical ionization) of I did not show a parent ion but indicated decomposition to $Fe(CO)_5$. The elemental analyses of I and other spectral results are, however, in good agreement with the proposed structure.

The reaction of triNC with 1 equiv of $Ru_3(CO)_{12}$ in C_6H_6 at room temperature with stirring for 24 h or at 50 °C for 3 h gives, in both cases, an orange-brown precipitate. Unfortunately, this product is insoluble in all common organic solvents and decomposes rapidly upon exposure to air. The reaction of triNC with equimolar $Os_3(CO)_{12}$ in heptane for 10 h gives a brown-orange precipitate which had properties very similar to those of the product obtained in the reaction of triNC with $Ru_3(CO)_{12}$.

It is known[7a] that $Co_2(CO)_8$ reacts with dilute RNC solutions under mild conditions to give tetrahedral clusters of the type $Co_4(CO)_{12-n}(RNC)_n$ (n = 2–4). It was hoped that triNC would coordinate to three Co atoms on a face of the tetrahedron. The slow dropwise addition at room temperature of a solution of triNC in C_6H_6 to a solution of $Co_2(CO)_8$ in the same solvent gives immediate precipitation of a yellow solid

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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 (λ = 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.

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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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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	ν, 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; λ_{max} (ϵ) 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).

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

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