Coordination Chemistry of the Bimacrocyclic, Potentially Binucleating Ligand 1,2-Bis(1,4,7-triaza-1-cyclononyl)ethane (dtne). Electrochemistry of Its First Transition Series Metal(II,III) Complexes. Characterization of the New Hemerythrin Model Complex [Fe₂(dtne)(μ-O)(μ-CH₃CO₂)₂]Br₂·H₂O

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A new synthesis for the hexadentate, potentially binucleating, bimacrocyclic ligand 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne) is reported, and its coordination chemistry with transition metals has been investigated. Mononuclear complexes [M(dtne)]³⁺ (M = Cr, Fe, Co, Ni) and [M′(dtne)]²⁺ (M′ = Mn, Ni, Cu, Zn) have been isolated as bromide, perchlorate, and hexafluorophosphate salts. Electronic spectra and effective magnetic moments have been measured. [Fe(dtne)]Br₃·3H₂O was found to have a low-spin electronic configuration. Formal redox potentials of the couples [M(dtne)]³⁺/²⁺ have been determined by cyclic voltammetry (Cr, –0.765 V; Mn, +0.88 V; Fe, +0.41 V; Co, –0.01 V; Ni, +1.10 V vs. NHE). Binuclear complexes (CO)₃M-(dtne)M(CO)₃ (M = Cr, Mo, W) have been prepared by reacting M(CO)₆ with dtne (2:1) in dmf. [Cl₃Fe(dtne)FeCl₃] reacts in an aqueous solution of sodium acetate to give the new hemerythrin model complex [Fe₂(dtne)(μ-O)(μ-CH₃CO₂)₂]Br₂·H₂O. Reactions of MnCl₂·4H₂O and CuCl₂·2H₂O with dtne (2:1) afford colorless [Cl₂Mn(dtne)MnCl₂] and blue [Cl₂Cu(dtne)CuCl₂]. The former is oxidized in alkaline solution by oxygen, yielding a tetrameric complex of Mn(IV): [Mn₄(dtne)₂(μ-O)₆]⁴⁺. The electrochemistry of [(tacn)Coᴵᴵᴵ(dtne)Coᴵᴵᴵ(tacn)]⁶⁺ has been investigated in detail. Two successive one-electron-transfer processes have been observed ($E_{1/2}^1 = +0.04$ V, $E_{1/2}^2 = –0.05$ V vs. NHE).

Introduction

The preparation of bimacrocyclic, N-donor ligands with binucleating properties toward transition metals has in recent years attracted much interest, and a variety of systems have been reported.[1,2] Fenton has recently reviewed this class of compounds, emphasizing their relevance to bioinorganic model systems.[3] One of the examples of such a binucleating ligand has been reported by Takamoto et al. in 1977,[4] although these authors did not recognize this property of their ligand, 1,4-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne), since mononuclear species with an

dtne
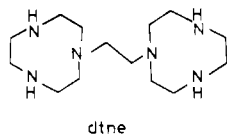
octahedral N₆ donor set are also formed. There are two cyclic triamine rings fused via an ethane bridge. The yields of the original synthesis appeared to be prohibitively low (~1%) for an extensive study of the ligating properties of this interesting ligand.

We have in the past made use of the unusually large kinetic and thermodynamic stability of complexes containing 1,4,7-triazacyclononane in order to generate oligomeric oxo- and/or hydroxo-bridged complexes of the early transition metals⁵⁻¹⁰ in various oxidation states. In an effort to further enhance the stability of binuclear species, we became interested in Takamoto's ligand. We here report a new synthesis affording the ligand in good yield and the synthesis of a series of mononuclear and oligomeric complexes.

At the outset of this investigation it was hoped that the ligand would occupy three coordination sites facially of two metal centers, respectively, forming binuclear species, which would then readily form M–X–M bridges with the remaining coordinating sites of

each metal ion, which are occupied in the first place by labile monodentate ligands.

Experimental Section

Abbreviations. 1,4,7-Triazacyclononane, tacn; 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane, dtne; 1,3-bis(1,4,7-triaza-1-cyclononyl)propane, dtnp; dimethylformamide, dmf; dimethyl sulfoxide, Me₂SO.

Preparation of Ligands. 1,4,7-Triazacyclononane was prepared by published methods.[11]

N,N′-Bis(p-tolylsulfonyl)-1,4,7-triazacyclononane. To 370 g of 1,4,7-triazacyclononane trihydrobromide dissolved in 750 mL of water was added 170 g of NaOH in small amounts with stirring and cooling. A 357-g amount of p-tolylsulfonyl chloride dissolved in 1.25 L of diethyl ether was added dropwise to this solution with vigorous stirring. Care was exercised to ensure that the reaction temperature was between 0 and 3 °C throughout this time. This mixture was stirred for another 1 h, and the temperature was allowed to rise to room temperature. The colorless precipitate was filtered, washed with large amounts of water, and dried at 105 °C. This crude product was always found to be contaminated with N,N′,N″-tris(p-tolylsulfonyl)-1,4,7-triazacyclononane. The crude material was extracted four to five times with 1 L of boiling ethanol. The first two fractions contained the major portions of the cyclic trisulfonamide——whereas from the last two fractions quite pure cyclic disulfonamide crystallized upon cooling. Recrystallization of the product obtained from the last three fractions from boiling ethanol gave a product that was satisfactorily used for further syntheses: mp 195–197 °C; yield ~70%.

The degree of contamination may be judged from ¹³C NMR spectra of the different sulfonamides. A table of ¹³C NMR data of these compounds is available as supplementary material.

1,2-Bis[N,N′-bis(p-tolylsulfonyl)-1,4,7-triaza-1-cyclononyl]ethane. A 110-g sample of N,N′-bis(p-tolylsulfonyl)-1,4,7-triazacyclononane and 46 g of 1,2-bis(p-tolylsulfonato)ethane were dissolved in 380 mL of dmf and stirred for 1 h at 105 °C. A 30-g amount of Na₂CO₃ was then added in small amounts with vigorous stirring. This solution was stirred mechanically at 120 °C for 18 h, after which time the solvent was removed under reduced pressure. The dry residue was suspended in 500 mL of boiling ethanol and poured into 2 L of ice/cold water. The colorless precipitate was filtered off, washed with water, and recrystallized from ethanol: mp 220–222 °C; yield 81%. The same procedure was used for the preparation of the propane derivative.

1,2-Bis(1,4,7-triaza-1-cyclononyl)ethane Hexahydrobromide Dihydrate. Fifty grams of the crude tetratosyl derivative was dissolved in 200 mL of concentrated H₂SO₄, and the mixture was heated with stirring at 110 °C for 48 h. After it was cooled to room temperature, this dark brown solution was added slowly (dropwise!) with cooling to 600 mL of ethanol; 250 mL of ice-cold ether was added, and the solution was allowed to stand in the refrigerator overnight. The brown precipitate was filtered off, washed with ether, and dissolved in a minimum amount of

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water. To this solution was added an equal volume of concentrated HBr (48%). When the mixture was cooled, a colorless precipitate formed, which was filtered off, washed with acetone, and air-dried; yield 80%. Anal. Calcd for $C_{14}H_{42}N_6Br_6O_2$: C, 20.87; H, 5.25; N, 10.43; Br, 59.49. Found: C, 21.0; H, 5.4; N, 10.4; Br, 59.4.

The same procedure was used to prepare 1,3-bis(1,4,7-triaza-1-cyclononyl)propane hexahydrobromide. Anal. Calcd for $C_{15}H_{40}N_6Br_6$: C, 22.98; H, 5.14; N, 10.72; Br, 61.12. Found: C, 23.1; H, 5.1; N, 10.7; Br, 61.2.

1,2-Bis(1,4,7-triaza-1-cyclononyl)ethane and 1,2-(1,4,7-triaza-1-cyclononyl)propane. A 0.5-mol amount of the respective hexahydrobromide was suspended in 150 mL of water, and 1 L of benzene was added. To the cooled solution (0 °C) was added with stirring and cooling 3.2 mol of NaOH dissolved in 150 mL of water. Then the water was removed by refluxing the water/benzene azeotrope with use of a water separator. When no more water separated, a further 5 g of NaOH was added to the suspension and refluxing was continued for 1 h. The suspension was filtered, and the precipitate was washed three times with 100 mL of hot benzene. From the combined filtrates the solvent was removed under reduced pressure. The resulting colorless oil crystallized within 12 h at room temperature; yield >85% for both ligands. ^{1}H NMR: for dtne in $CDCl_3$, $\delta(CH_2)$ 2.68 m (28 H), δ (NH) 2.17 s (4 H); for dtnp in $CDCl_3$, δ 2.71 s (8 H), δ 2.61 m (24 H), $\delta(NH)$ 2.49 s (4 H).

Preparation of Complexes. A table containing data of elemental analyses (C, H, N, halide, metal) is available as supplementary material.

[Cr(dtne)]Br$_3$·0.5H$_2$O. The volume of a solution of 0.5 g of $CrCl_3$·$6H_2O$ in 10 mL of Me_2SO was reduced at 190 °C to 5 mL by evaporation. One gram of the ligand dtne was dissolved in 5 mL of Me_2SO. These two solutions were combined at 130 °C and stirred for 15 min at 190 °C. The volume of this solution was reduced to 5 mL on a rotary evaporator under reduced pressure. Orange crystals precipitated at room temperature, which were filtered off, washed with ether, and air-dried. From an aqueous solution of the above chloride salt the perchlorate or bromide salts were obtained upon addition of solid $NaClO_4$ or NaBr, respectively; yield 65%.

[Cl$_3$Cr(dtne)CrCl$_3$]·H$_2$O. When the above solution of $CrCl_3$·$6H_2O$ in Me_2SO was treated with a solution of only 0.28 g of dtne in 5 mL of Me_2SO at 130 °C for 75 min, a green precipitate of the desired binuclear complex was obtained; yield 42%.

[(CO)$_3$Cr(dtne)Cr(CO)$_3$]·H$_2$O. To an argon-scrubbed solution of 0.57 g of dtne in 50 mL of dry dmf was added 1.1 g of $Cr(CO)_6$. The solution was refluxed for 30 min. A yellow precipitate was filtered off after cooling (20 °C), washed with hot toluene, and air-dried; yield 73%.

[(CO)$_3$Mo(dtne)Mo(CO)$_3$] and [(CO)$_3$W(dtne)W(CO)$_3$]. These binuclear complexes of molybdenum and tungsten were prepared analogously from $Mo(CO)_6$ and $W(CO)_6$, respectively.

[Br$_3$Cr(dtne)CrBr$_3$]. To a boiling suspension of 1.1 g of [(CO)$_3$Cr(dtne)Cr(CO)$_3$] in dry chloroform under an argon atmosphere was added dropwise with stirring 1 g of bromine. The suspension was refluxed for 5 h. The then green precipitate was filtered off, washed with ether, and air-dried; yield 85%.

[Cl$_2$Mn(dtne)MnCl$_2$]·0.5H$_2$O. The volume of a boiling solution of 0.39 g of $MnCl_2$·$4H_2O$ in 20 mL of dry ethanol was reduced to 10 mL by evaporation, and a solution of 0.28 g of dtne dissolved in 10 mL of ethanol was added in small amounts. A colorless precipitate formed immediately, which was filtered off and air-dried; yield 89%.

[Mn(dtne)](PF$_6$)$_2$. To a solution of 1.1 g of [Cl$_2$Mn(dtne)MnCl$_2$] in 15 mL of water was added 2 g of NaPF$_6$ at room temperature. A colorless precipitate formed, which was filtered off, washed with ethanol and ether, and air-dried; yield 36%.

[Mn$_4$(dtne)$_2$O$_6$](ClO$_4$)$_4$. To 0.72 g of $Mn(ClO_4)_2$·$6H_2O$ dissolved in 30 mL of ethanol was added dropwise under reflux a solution of 0.28 g of dtne in 20 mL of ethanol. When this solution was allowed to stand for 5 days in an open vessel at room temperature or a stream of oxygen was slowly bubbled through the solution for 1 day at 20 °C, a black precipitate formed, which was filtered off, washed with ethanol and ether, and air-dried; yield 46%.

[Fe(dtne)]Br$_3$·3H$_2$O. A 0.92-g amount of $Fe(ClO_4)_3$·$6H_2O$ was dissolved in 20 mL of dry ethanol. A 0.57-g sample of dtne dissolved in 10 mL of ethanol was added dropwise under reflux within 6 h to this solution. The precipitate obtained was filtered off and dissolved in a minimum amount of water. Two grams of solid NaBr was added with stirring. Red crystals precipitated, which were filtered off, washed with ethanol and water, and air-dried; yield 63%.

[Cl$_3$Fe(dtne)FeCl$_3$]. This complex was prepared by following the procedure described for the preparation of [Cl$_3$Cr(dtne)CrCl$_3$] using 0.54 g of $FeCl_3$·$6H_2O$ and 0.29 g of dtne; yield 71%.

[Fe$_2$(dtne)(μ-O)(μ-CH$_3$CO$_2$)$_2$]Br$_2$·H$_2$O. To a solution of 6.2 g of sodium acetate in 20 mL of water was added with stirring 0.5 g of [Cl$_3$Fe(dtne)FeCl$_3$]. After 30 min at 20 °C, 10 mL of a saturated

aqueous solution of NaBr was added to the then clear, deep brown solution. When the solution was allowed to stand in an open vessel for 24 h, brown crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried; yield 32%.

[Co(dtne)]Br$_3$·3H$_2$O. A solution of 0.92 g of [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$ and 0.57 g of dtne in 50 mL of water was stirred 4 h at 90 °C, after which time the volume of the solution was reduced to 25 mL. Upon addition of 2 g of NaBr and cooling (10 °C), red crystals precipitated, which were twice recrystallized from water; yield 78%.

[Cl$_3$Co(dtne)CoCl$_3$]. To a solution of 1.62 g of Na$_3$[Co(NO$_2$)$_6$] in 50 mL of water was added dropwise (2 h) with stirring 10 mL of an aqueous solution of 0.57 g of dtne. This solution was stirred for 2 days at 80 °C. The orange-brown precipitate of [(NO$_2$)$_3$Co(dtne)Co(NO$_2$)$_3$] was filtered off, washed with ethanol and ether, and air-dried. A suspension of 0.9 g of this material in 50 mL of concentrated HCl was stirred at room temperature at 40 °C for 30 min. The green precipitate was filtered off, washed with ethanol, and air-dried; yield 31%.

[Co(dtnp)](ClO$_4$)$_3$·1.5H$_2$O. This complex has been obtained in 70% yields with use of the procedure described for [Co(dtne)]Br$_3$·3H$_2$O with 1.4 g of [Co(NH$_3$)$_5$OH$_2$](ClO$_4$)$_3$, 0.9 g of dtnp, and solid $NaClO_4$ instead of NaBr.

[(tacn)Co(dtne)Co(tacn)]Br$_6$·6H$_2$O. To a suspension of 1.2 g of green [Co(tacn)Cl$_3$]^{11b} in 50 mL of dry isopropyl alcohol under reflux was added dropwise a solution of 0.57 g of dtne in 20 mL of isopropyl alcohol. The solution was refluxed until a clear brown solution was obtained. Under reduced pressure the volume of the solution was reduced to 15 mL and cooled (5 °C). The brown precipitate was filtered off and recrystallized from a minimum amount of water by addition of solid NaBr. The product was further purified by chromatography with a Sephadex SP-C 25 cation-exchange column. The desired red complex was eluted with 1 M HBr; yield 71%.

[Ni(dtne)](ClO$_4$)$_2$·2H$_2$O. To a solution of 0.73 g of $Ni(ClO_4)_2$·$6H_2O$ in 20 mL of ethanol was added dropwise under reflux 0.57 g of dtne dissolved in 20 mL of ethanol. A red precipitate formed immediately, which was filtered off and recrystallized from water and $NaClO_4$; yield 83%.

[Ni(dtne)](ClO$_4$)$_3$·3H$_2$O. To a solution of 0.58 g of [Ni(dtne)](ClO$_4$)$_2$·2H$_2$O dissolved in 10 mL of 10^{-3} M perchloric acid was added solid $Na_2S_2O_8$ (1.6 g) at 2 °C. This solution was stirred for 10 min at 2 °C and with exclusion of light, after which time 2 mL of a saturated aqueous solution of $NaClO_4$ was added. A yellow-green precipitate was obtained, which was filtered off, washed with ether (rapidly), and air-dried. The complex is light sensitive and decomposes slowly upon storage even when kept in the dark; yield 43%.

[Cu(dtne)](ClO$_4$)$_2$. This blue complex has been obtained with use of the procedure described for the preparation of [Ni(dtne)](ClO$_4$)$_2$·2H$_2$O. It was recrystallized from ethanol and $NaClO_4$; yield 79%.

[Cl$_2$Cu(dtne)CuCl$_2$]·1.5H$_2$O. To a solution of 0.34 g of $CuCl_2$·$2H_2O$ in 15 mL of ethanol was added dropwise under reflux a solution of 0.28 g of dtne dissolved in 10 mL of ethanol. A blue precipitate formed, which was filtered off, washed with ethanol and ether, and air-dried; yield 74%.

[Zn(dtne)](ClO$_4$)$_2$·H$_2$O. This colorless complex has been obtained with use of the procedure described for the preparation of [Ni(dtne)](ClO$_4$)$_2$·2H$_2$O.

Electrochemistry. The apparatus used has been described elsewhere.[12] Cyclic voltammograms and differential pulse voltammograms were measured with a platinum (0.071 cm^2), glassy-carbon (0.196 cm^2), or hanging-mercury-drop electrode (0.010 cm^2) using the Model 303 A static mercury drop electrode with the PAR M 264 A combined programmer/potentiostat. A Pt-wire auxiliary electrode and a reference electrode (Ag/AgCl in saturated NaCl or KCl) were used. In general, argon-scrubbed solutions of the supporting electrolyte (0.1 or 0.2 M) containing 10^{-3} M of sample were investigated at 25 °C.

Interpretations of cyclic voltammograms were performed with use of diagnostic criteria derived by Nicholson and Shain.[13] Differential pulse voltammograms were evaluated according to Parry and Osteryoung.[14] The electrochemistry of the binuclear cobalt(III) complex [Co$_2$(dtne)(tacn)$_2$]$^{6+}$ is more complex, and special methods for the interpretation were used following procedures outlined by Richardson and Taube.[15]

Potentials were corrected to the normal hydrogen electrode (NHE) by adding 0.200 V to the measured potential.

Magnetic Measurements. The magnetic susceptibilities of powdered samples were measured by using the Faraday method, and diamagnetic

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Table I. Electronic Spectra and Effective Magnetic Moments of Complexes Containing the Ligand 1,2-Bis(1,4,7-triaza-1-cyclononyl)ethane (L)

complex	color	λ, nm (ϵ, L mol^{-1} cm^{-1})	μ_{eff}(20 °C), μ_B
		A. Mononuclear Complexes	
$[CrL]^{3+}$	orange	360 (142), 481 (280)	3.8
$[MnL]^{2+}$	colorless		5.9
$[FeL]^{3+}$	red	355 (772), 457 (464)	2.7
$[CoL]^{3+}$	orange	346 (230), 495 (323)	diamag
$[NiL]^{2+}$	blue	363 (16), 516 (18), 848 (31), 917 (31)	3.1
$[NiL]^{3+}$	orange-green	311 (9 × 10^3), 623 (62), 1020 (12)	not measd
$[CuL]^{2+}$	blue	646 (126)	2.2
		B. Oligomeric Complexes	
$[Co_2L(tacn)_2]^{6+}$	orange	343 (293),^{a} 492 (324)^a	diamag
$[Fe_2LCl_6]$	yellow		5.6^b
$[Cu_2LCl_4]$	blue		2.0^b
$[Mn_4L_2O_6]^{4+}$	red	331 (5.2 × 10^3),^{c} 551 (9.1 × 10^2)^c	3.9^b
$[Fe_2L(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}$	brown	322 (6.8 × 10^3),^{a} 415 (8.7 × 10^2), 488 (4.5 × 10^2), 656 (130)	

^{a} Molar absorption coefficient per dimer. ^{b} Per metal center. ^{c} Molar absorption coefficient per tetramer.

Scheme I
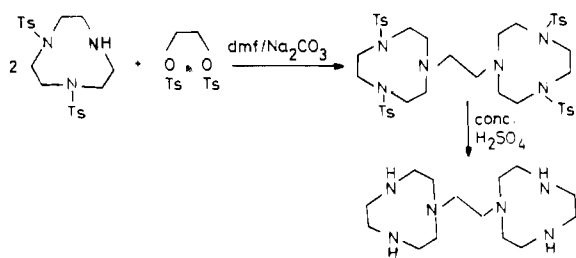
corrections were applied with use of published tables.

Results and Discussion

Preparation of Ligands. The ligand 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane (dtne) has been synthesized in good yield with use of N,N'-bis(p-tolylsulfonyl)-1,4,7-triazacyclononane, which was reacted with 1,2-bis(p-tolylsulfonato)ethane. The resulting 1,2-bis[N,N'-bis(p-tolylsulfonyl)-1,4,7-triaza-1-cyclononyl]ethane was treated with concentrated sulfuric acid, affording a polyhydrosulfate salt that is free of p-tolylsulfonyl groups.

The analogous 1,2-bis(1,4,7-triaza-1-cyclononyl)propane has been prepared with use of 1,3-bis(p-tolylsulfonato)propane. The polyhydrosulfates were dissolved in water and recrystallized as hexahydrobromides by addition of concentrated hydrobromic acid (Scheme I).

Mononuclear Complexes. The reaction of equimolar amounts of dtne with transition-metal(II,III) salts in various solvents such as Me$_2$SO, ethanol, and water affords extremely stable mononuclear complexes. [M(dtne)]$^{n+}$ species with $n = 2,3$ have been isolated as bromide, hexafluorophosphate, and perchlorate salts (M = Cr(III), Mn(II), Fe(III), Co(III), Ni(II), Ni(III), Cu(II), Zn(II)). The ligand is a hexadentate N$_6$ donor with four secondary and two tertiary amine nitrogens, which are coordinated pseudooctahedrally to the respective metal center. A ball and stick representation of such a complex is shown in Figure 1. Electronic spectra and effective magnetic moments of complexes are summarized in Table I. The electronic spectra are in all cases as can be expected for a given d^n electronic configuration of the metal center in an octahedral N$_6$ environment. Three observations merit further comment.

(1) In general, the molar absorption coefficients, ϵ (in L mol^{-1} cm^{-1}), of d–d transitions of [M(dtne)]$^{n+}$ species are unexpectedly large. Thus, the first transition ($^1A_1$–$^1T_1$) for [Co(dtne)]$^{3+}$ has an ϵ of 323 whereas the corresponding value for [Co(tacn)$_2$]$^{3+}$ is only 100[12] and Sargeson's cage complex [Co(sep)]$^{3+}$ exhibits an ϵ of 109 for this d–d transition.[16]

Furthermore, the Co^{III}N$_6$ complex containing two N-methyl-1,4,7-triazacyclononane rings—the ligand has one tertiary and
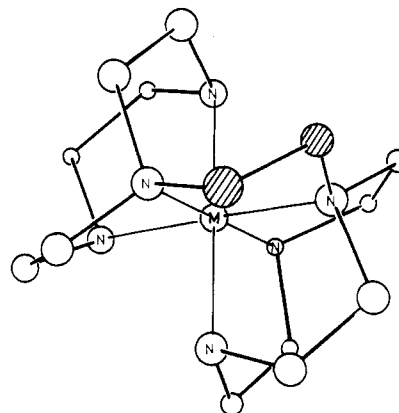

Figure 1. Ball and stick representation of a mononuclear [M(dtne)]$^{n+}$ species (carbon atoms of the ethane bridge are shaded).

two secondary amine nitrogens—shows absorption maxima at 348 nm ($\epsilon = 145$, $^1A_1$–$^1T_2$) and at 510 nm ($\epsilon = 162$, $^1A_1$–$^1T_1$).[17] This indicates that in addition to an electronic factor induced via the tertiary amine nitrogens, a steric factor is likely to be responsible for the large molar absorption coefficient in [Co(dtne)]$^{3+}$. Indeed, molecular models indicate that the ethane bridge of dtne may enforce a trigonal twist of two 1,4,7-triazacyclononane moieties with respect to each other ($\vartheta < 60°$):
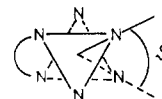
The octahedral symmetry of the N$_6$ donors is distorted.

(2) The electronic spectra of [Ni(tacn)$_2$]$^{2+}$ [18] and [Ni(dtne)]$^{2+}$ are very similar. It is concluded that the ligand field strength of dtne is also very similar to that of the very strong ligand tacn ($Dq = 1140$ cm^{-1} and $B = 980$ cm^{-1}).[18] In good agreement with this observation, the [Fe(dtne)]$^{3+}$ complex was found to be a low-spin complex of Fe(III) as is [Fe(tacn)$_2$]$^{3+}$.[12,19] These two species are the only low-spin Fe(III) complexes with a saturated N$_6$ donor set known to date.

(3) Oxidation of [Ni(dtne)]$^{2+}$ in 10^{-3} M HClO$_4$ with Na$_2$S$_2$O$_8$ at 2 °C leads to a greenish brown solution from which upon addition of NaClO$_4$ the solid [Ni(dtne)](ClO$_4$)$_3$ has been obtained. The complex is light sensitive and decomposes even in the solid state within hours. The electronic spectrum is similar to that of [Ni(tacn)$_2$](ClO$_4$)$_3$. In contrast to McAuley's report[20] on the

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electronic spectrum of $[Ni(tacn)_2]^{3+}$, we do observed d–d transitions in the visible region of low intensity for both Ni(III) complexes.[12] It is concluded that a genuine Ni(III) species is formed. From the cyclic voltammogram (see below) it is seen that this is a very strong one-electron oxidant.

Oligomeric Complexes. The reaction of $M(CO)_6$ (M = Cr, Mo, W) with dtne (2:1) in dmf yields air-stable binuclear, neutral complexes, $[(CO)_3M(dtne)M(CO)_3]$. The two subunits may take up any orientation between the two extreme syn and anti arrangements because the ethane bridge is flexible and the metal centers are not connected via other bridging ligands:

syn

anti
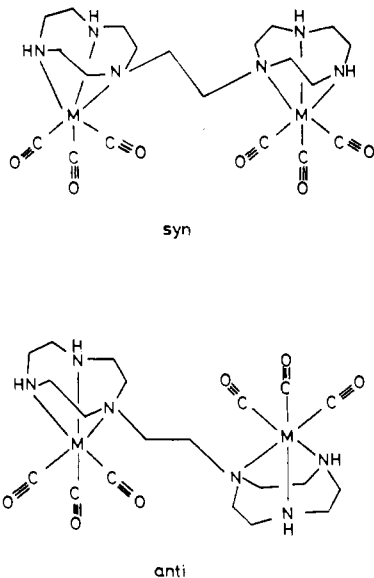
These complexes are useful starting materials for the syntheses of binuclear species with the metal centers in higher oxidation states via oxidative decarbonylation reactions. This concept has been described previously for mononuclear $[(tacn)M(CO)_3]$ complexes.[21] For example, the reaction of $[(CO)_3Cr(dtne)Cr-(CO)_3]$ with bromine in chloroform affords $[Br_3Cr(dtne)CrBr_3]$. This type of complex was also generated directly from metal(III) chlorides and dtne (2:1), $[Cl_3M(dtne)MCl_3]$ (M = Cr(III), Fe(III), Co(III)).

Reacting $MnCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 2H_2O$ dissolved in ethanol with dtne (2:1) yields binuclear complexes $[Cl_2Mn(dtne)MnCl_2]$ and $[Cl_2Cu(dtne)CuCl_2]$, respectively. In both cases the metal centers attain the coordination number 5. It is noted that such mononuclear species have been characterized for $[Cu(tacn)X_2]$ (X = Cl, Br) by X-ray crystallography.[22,23]

In agreement with the proposed structures are the effective magnetic moments of $[Cl_2Cu(dtne)CuCl_2]$ and $[Cl_3Fe(dtne)-FeCl_3]$ (Table I), which exhibit normal Curie–Weiss behavior over the temperature range 93–293 K for each metal center, and no indication for intramolecular spin coupling has been observed. The binuclear iron(III) complex exhibits the characteristic magnetic moment per iron center for a high-spin d^5 electronic configuration as do the Cu(II) centers for a d^9 configuration in $[Cl_2Cu-(dtne)CuCl_2]$.

The binuclear carbonyl and halo complexes are excellent starting materials for the preparation of oxo- and/or hydroxo-bridged binuclear species. This may be exemplified by the following two reactions. The syntheses of other such complexes are presently being studied in depth in this laboratory and will be communicated.

Hydrolysis of $[Cl_3Fe(dtne)FeCl_3]$ in aqueous solution containing sodium acetate yields a clear brown solution, from which upon

addition of solid sodium bromide brown crystals of $[Fe_2(dtne)-(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2]Br_2 \cdot 2H_2O$ were isolated:
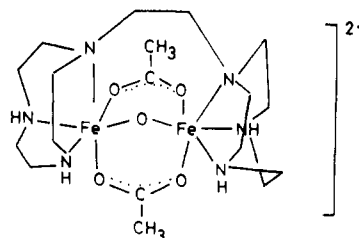
In the IR spectrum two bands due to bridging acetate groups are observed at $\nu_{as}(CO) = 1530$ cm^{-1} and $\nu_1(CO) = 1420$ cm^{-1}. The electronic spectrum (Table I) is very similar to that observed for $[Fe_2(tcan)_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2]^{2+}$. The latter complex has been shown by X-ray crystallography to contain a μ-oxo bridge and two bridging acetate groups.[10] This type of complex has recently attracted considerable interest as model compounds for the enzyme hemerythrin.[24,25] The unique feature of this complex is that the two tridentate 1,4,7-triazacyclononane subunits are connected by an ethane bridge. This may prevent rapid decomposition of the complex in its *reduced* form in solution and may provide a model for the active enzyme, although—in contrast to the case for the enzyme—no labile coordination site at either Fe(II) center would be present.

A second example for the usefulness of complexes containing the ligand 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane for the preparation of oligomeric oxo-bridged species is the reaction of $Mn^{II}(ClO_4)_2$ and the ligand (2:1) in alkaline solution in the presence of air. Slowly a black precipitate of $[Mn_4(dtne)_2O_6]-(ClO_4)_4$ is obtained.

In the infrared an intense band at 730 cm^{-1} is characteristic of vibrations of the Mn_4O_6 cluster. This band has also been observed for $[Mn_4(tacn)_4O_6]Br_{3.5}OH_{0.5} \cdot 6H_2O$ (and for its tetraperchlorate salt), the structure of which has been determined by X-ray crystallography.[8] The electronic spectra of both complexes are also very similar. Therefore, we propose the adamantane-like structure
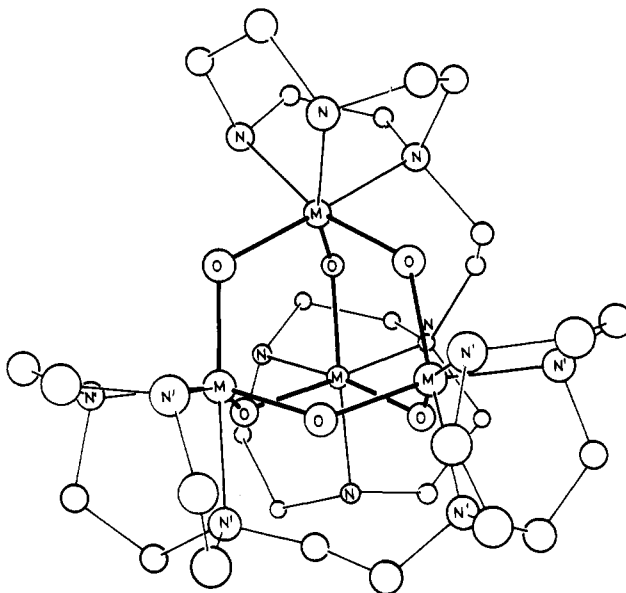
for this complex. The complex is stable in neutral and alkaline aqueous solution. This complex is a further example for stable, rare oligomeric Mn(IV) species. Compounds of this type are of interest in connection with certain enzymes for photosynthesis, which are capable of oxidizing water.[26]

(21) Chaudhuri, P.; Wieghardt, K.; Tsay, Y. H.; Krüger, C. *Inorg. Chem.* **1984**, *23*, 427.

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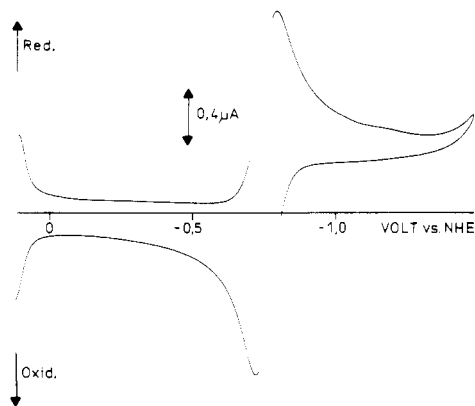
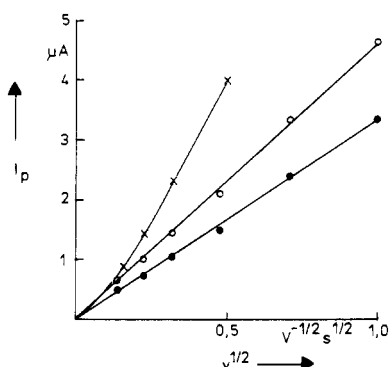**Figure 2.** Cyclic voltammograms of $[Cr(dtne)]^{3+}$ (scan rate 0.1 V s^{-1}, $c = 0.79$ mmol L^{-1}, 0.1 M [TMA]Br, HMDE).

Figure 3. Plot of peak current, I_p, vs. scan rate $(v^{1/2})$ for $[Cr(dtne)]^{2+/3+}$ (O), $[Co(dtne)]^{2+/3+}$ (●), and $[Mn(dtne)]^{3+/2+}$ (×).

Finally, we have isolated a binuclear complex of cobalt(III), where the two metal centers have an N$_6$ donor set, reacting $[Co(tacn)Cl_3]^{11b}$ with dtne (2:1). Two octahedrally coordinated metal centers are connected via an ethane bridge in $[(tacn)Co-(dtne)Co(tacn)]^{6+}$.

Electrochemistry of Mononuclear Complexes. Cyclic voltammograms of mononuclear $[M(dtne)]^{n+}$ species (M = Cr, Mn, Fe, Co, Ni) exhibit one oxidation–reduction wave in the potential range +1.40 to −1.50 V vs. NHE:

$$[M^{III}(dtne)]^{3+} + e^- \rightleftarrows [M^{II}(dtne)]^{2+}$$

$$M = Cr, Mn, Fe, Co, Ni$$
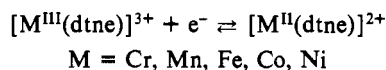
Figure 2 shows a typical example. Diagnostic criteria (Table II)
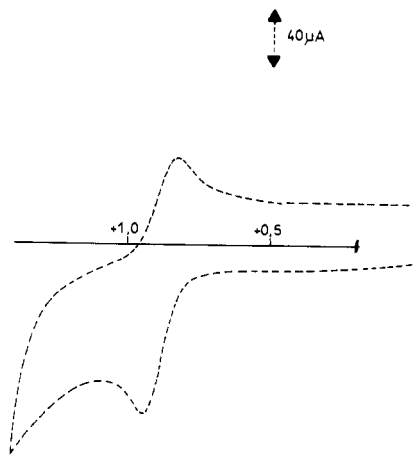
Table II. Electrochemical Data of the Redox Couple $[M(dtne)]^{3+/2+}$ in 0.1 M LiClO$_4$ at 25 °C

couple	elec-trode	E^f, V vs. NHE	ΔE_p, mV^a	$I_{p,b}/I_{p,f}$	cf^b	cf'^{c}
$[Cr(dtne)]^{3+/2+}$	HMDE	−0.765	71	0.95	5.8	0.58
$[Mn(dtne)]^{3+/2+}$	GC	+0.88^d	105	0.7	125	0.64
$[Fe(dtne)]^{3+/2+}$	GC	+0.41	78	1.1	140	0.71
$[Co(dtne)]^{3+/2+}$	HMDE	−0.01	69	1.0	5.2	0.52
$[Ni(dtne)]^{3+/2+}$	Pt	+1.10	85		52	0.73

^{a} Peak potential difference at a scan rate of 0.05 V s^{-1}. ^{b} Current function of the oxidation peak, in μA V$^{-1/2}$ s$^{1/2}$ mmol^{-1} L. ^{c} Peak current function corrected for electrode surface, in A V$^{-1/2}$ s$^{1/2}$ mol^{-1} cm. ^{d} Measured at 4 °C.

indicate a chemically reversible one-electron process. The peak potential differences, ΔE_p, are somewhat larger than the theoretical value of 57 mV. It is a common observation that values of ΔE_p are larger than the theoretical value at planar solid-state electrodes in aqueous solution due to hindered electrode kinetics of the electron transfer with increasing scan rates.

The cyclic voltammogram of $[Mn(dtne)]^{2+}$ is more complicated. At 25 °C this species is oxidized to the Mn(III) species. The intensity of the oxidation peak is independent of the scan rate. In contrast, the reduction peak varies strongly in both position and intensity with the scan rate. The current function increases with increasing scan rate (Figure 3) in conjunction with an increasing peak current ratio, $I_{p,b}/I_{p,f}$. This clearly indicates a chemical change of the oxidized species.

This is also nicely demonstrated by repeated cyclic voltammetric scans at 4 °C (Figure 4). This behavior has also been reported for the analogous couple $[Mn(tacn)_2]^{3+/2+}$.[12]

The formal redox potentials of the five couples $[M(dtne)]^{3+/2+}$ embrace a wide potential range. Figure 5 shows the formal redox potentials of couples $[M(dtne)]^{3+/2+}$ and $[M(tacn)_2]^{3+/2+}$ as a function of the d^n electronic configuration of the respectively metal center. For all complexes the potentials of dtne complexes are more positive (+0.3 V) than for the corresponding complexes with two tacn ligands. Two factors may account for this behavior. One is the electronic factor, which stems from the substitution of two secondary amine nitrogens in $[M(tacn)_2]^{n+}$ species for two tertiary amine nitrogens in $[M(dtne)]^{n+}$ complexes, which stabilize the reduced species. In addition, a steric factor also contributes. As suggested before, in mononuclear complexes of $[M(dtne)]^{3+}$ the bridging ethane group exerts some additional strain, which is somewhat relieved in their reduced forms due to the increased ionic radii of the metal(II) centers. This is nicely demonstrated by the formal redox potential of −0.095 V measured for the $[Co(dtnp)]^{3+/2+}$ couple. The propane bridge is more flexible than the ethane bridge, and the redox potential is shifted to a value

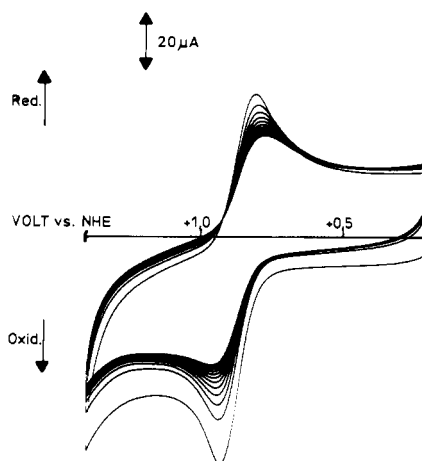**Figure 4.** Cyclic voltammograms of $[Mn(dtne)]^{3+/2+}$ at 25 (- - -) and 4 °C (—) in 0.1 M LiClO$_4$ and at a scan rate of 0.05 V s^{-1} (Pt electrode, $c = 2.08$ mmol L^{-1}).

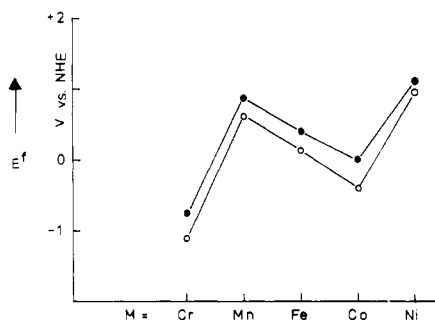**Figure 5.** Redox potentials of the couples $[M(tacn)_2]^{3+/2+}$ (O) and [M-(dtne)]$^{3+/2+}$ (●) as a function of the d^n electronic configuration of M.
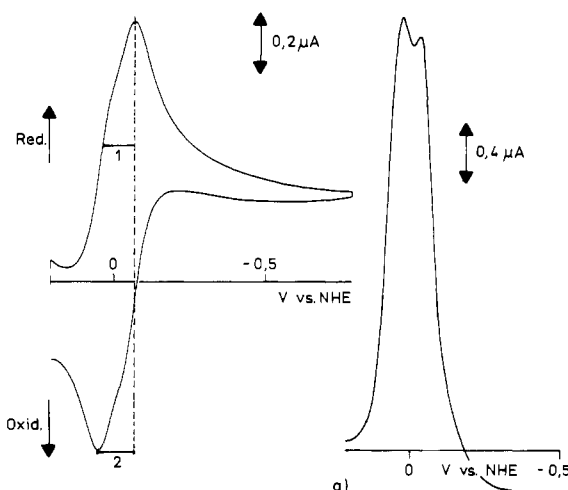

Figure 6. Cyclic voltammogram of $[(tacn)Co(dtne)Co(tacn)]^{6+}$ (left-hand side; c = 0.36 mmol L^{-1} in 0.2 M KCl, 25 °C, HMDE, v = 0.050 V s^{-1}) and its differential pulse voltammogram (right-hand side; SMDE, pulse amplitude 25 mV, v = 1 mV s^{-1}, c = 0.23 mmol L^{-1}).

more negative than that of $[Co(dtne)]^{3+/2+}$.

Electrochemistry of $[(tacn)Co(dtne)Co(tacn)]^{6+}$. The cyclic voltammogram of the binuclear complex $[(tacn)Co(dtne)Co(tacn)]^{6+}$ in aqueous solution is shown in Figure 6. In the potential range between +0.20 and −0.80 V one reduction and one oxidation peak is observed. The cyclic voltammogram exhibits two shoulders at the reduction peak and at the oxidation peak, respectively, which indicates a superposition of two redox waves at similar potentials. The form and position of the cyclic voltammogram do not change upon repeated scanning, indicating chemical reversibility of the observed redox processes.

Coulometric measurements at −0.5 V indicate a transfer of two electrons per dimer.

Assuming then that $[(tacn)Co(dtne)Co(tacn)]^{6+}$ is reduced in two successive one-electron-transfer steps, two redox potentials may be evaluated with use of the procedure described by Richardson and Taube.[15] This has been done for three different scan rates, yielding $E_{1/2}^1$ = +0.04 V and $E_{1/2}^2$ = −0.05 V. The peak current ratio, $I_{p,ox}/I_{p,red}$, of 1.05 is constant at scan rates 0.02–0.50 V s^{-1}, indicating chemical stability of the reduced and oxidized species in solution at least on the time scale of cyclic voltammetry.

It also demonstrates the kinetic reversibility of the electron-transfer processes. These observations justify the treatment of data according to ref 15.

Thus the following redox scheme is set up:

$$[(tacn)Co^{III}(dtne)Co^{III}(tacn)]^{6+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$

$$[(tacn)Co^{II}(dtne)Co^{III}(tacn)]^{5+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}}$$
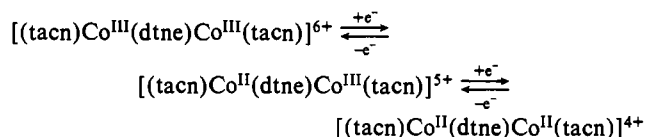
$$[(tacn)Co^{II}(dtne)Co^{II}(tacn)]^{4+}$$

Figure 6 shows the differential pulse voltammogram of the binuclear cobalt(III) species, which exhibits two well-resolved peaks of nearly identical intensity. From this voltammogram the two redox potentials E_1 and E_2 were evaluated to be +0.03 and −0.055 V, in excellent agreement with the above values from cyclic voltammetry measurements.

From the difference of the two redox potentials, $E_{1/2}^1 - E_{1/2}^2$ = 90 mV, a comproportionation constant, K_c, of 30 is calculated:

$$Co^{III}_2 + Co^{II}_2 \overset{K_c}{\rightleftharpoons} 2[Co^{III}Co^{II}]$$
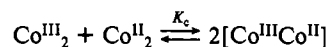
As Gagné and Spiro[27] have pointed out, noninteracting metal sites will have $E_1 - E_2$ = 36 mV, attributable to the simple statistical factor $RT/F \ln 4$, if the two metal ions have identical inherent reduction potentials.

As the metals come closer together, which is enforced by the steric demands of the ligand dtne, electrostatic interactions become important, yielding $E_1 - E_2$ > 36 mV. The measured value of 90 mV appears to reflect this effect rather than an electronic delocalization, which would also stabilize the mixed-valence $Co^{III}Co^{II}$ species.[28]

Supplementary Material Available: Tables of elemental analyses (C, H, N, halogens, metal) and ^{13}C NMR data of the macrocyclic polyamines and their precursors (3 pages). Ordering information is given on any current masthead page.

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