$(OCH_3)_2$, MnTPP$(OCD_3)_2$, and C_6H_5I (Figure S1), variable-temperature magnetic susceptibility data (Table SI) and details of calculations, crystallographic data including anisotropic thermal parameters for non-hydrogen atoms (Table SII), observed and calculated structure factor amplitudes (Table SIII), final hydrogen atom positional and thermal parameters (Table SIV), least-squares planes (Table SV), and intermolecular contacts (Table SVI) (22 pages). Ordering information is given on any current masthead page.

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1,4,7-Triazacyclononane-*N*,*N*′,*N*″-triacetate (TCTA), a Hexadentate Ligand for Divalent and Trivalent Metal Ions. Crystal Structures of [Cr^{III}(TCTA)], [Fe^{III}(TCTA)], and Na[Cu^{II}(TCTA)]·2NaBr·8H$_2$O

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Received April 28, 1982

Monomeric complexes of di- and trivalent metal ions containing the potentially hexadentate ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (TCTA) have been synthesized: [M^{III}(TCTA)], M = Al, Cr, Mn, Fe, Co, and [M^{II}(TCTA)]$^-$, M = Mn, Fe, Co, Ni, Cu. The crystal structures of [Cr^{III}(TCTA)] (**1**), [Fe^{III}(TCTA)] (**2**), and Na[Cu^{II}(TCTA)]·2NaBr·8H$_2$O (**3**) have been determined by single-crystal X-ray diffraction. Crystals of **1** were monoclinic with space group C_{2h}^5-$P2_1/n$ (a = 8.825 (9) Å, b = 13.458 (7) Å, c = 11.913 (12) Å, β = 106.09 (10)°, Z = 4, V = 1360 Å^3). The structure consists of neutral complexes of [Cr(TCTA)] with a chromium(III) ion in a distorted-octahedral environment of a facial N_3O_3 donor set. Crystals of **2** were rhombohedral with space group C_{3v}^6-$R3c$ (a = 13.577 (3) Å, Z = 6, V = 2117 Å^3). The neutral molecules of [Fe^{III}(TCTA)] have crystallographically imposed C_3 symmetry. The iron(III) ions are in a distorted-pseudoprismatic environment. Crystals of **3** were triclinic with space group C_i^1-$P\bar{1}$ (a = 9.156 (1) Å, b = 11.679 (3) Å, c = 14.131 (2) Å, α = 104.14 (2)°, β = 103.81 (1)°, γ = 102.74 (2)°, Z = 2, V = 1388 Å^3). The structure consists of two monoanions of [Cu^{II}(TCTA)]$^-$, sodium and uncomplexed bromide ions, and molecules of water of crystallization. The Cu(II) ions are in a highly distorted pseudoprismatic environment of N_3O_3 donor atoms. The visible absorption spectra, magnetic moments, and pertinent infrared data are described. Formal reduction potentials for the couples [Cr(TCTA)]$^{0/-}$, [Mn(TCTA)]$^{0/-}$, [Fe(TCTA)]$^{0/-}$, [Co(TCTA)]$^{0/-}$, and [Ni(TCTA)]$^{0/-}$ vs. the normal hydrogen electrode have been determined from their reversible cyclic voltammograms (−1.17, +0.80, +0.195, 0.00, and +1.16 V, respectively).

Introduction

Syntheses for tetraaza macrocycles with four N-bonded acetate groups have recently been published.[2-4] The stabilities of metal complexes containing these EDTA analogues appear to be large and in some cases even larger than are observed for the corresponding EDTA complexes.[2-4] Kaden et al.[3] have proposed that these potentially octadentate ligands coordinate metal ions such as Cu(II) and Ni(II) in a pseudooctahedral fashion where only two nitrogen atoms of the ligand and two oxygens of the carboxylate groups are bound to the metal centers.

In view of the propensity of most divalent and trivalent transition-metal ions for the coordination number 6 we have synthesized the ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate. This ligand is ideally suited to be wrapped around metal ions. It is to be expected that the first and second coordination spheres of such complexes should change only slightly in some instances when the oxidation state of the metal center is increased or decreased by 1 unit via outer-sphere electron-transfer reactions. Therefore, we believe that a series of such complexes is ideally suited for delineating factors governing the electron-transfer rates of outer-sphere reactions in homogeneous solutions. We report here the preparation and structural characterization of these complexes containing the ligand.

Experimental Section

Preparation of the Ligand. The starting compound 1,4,7-triazacyclononane trihydrobromide was prepared according to a modified method[5] described by Atkins and co-workers.[6] Aqueous solutions containing the ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (TCTA) were prepared by following procedures reported for the syntheses of similar tetraaza tetraacetate macrocycles.[2-4] To a solution of 37.1 g of 1,4,7-triazacyclononane trihydrobromide (0.1 mol) and 12.0 g of NaOH (0.3 mol) in 35 mL of water was added with stirring at 20 °C a second solution containing 47.2 g of bromoacetic acid (0.3 mol) and 12.0 g of NaOH in 100 mL of water. The temperature was raised to 80 °C, and 12.0 g of NaOH dissolved in 65 mL of water was added dropwise. The temperature was maintained at 80 °C for 1 h, after which time the reaction was completed. The pH of the solution was adjusted to 7 with concentrated HBr. Attempts to isolate a crystalline sodium salt of the ligand or the uncomplexed acid from such solutions at pH 12, 7, 2.5, and 1 have failed. Portions of the above solution were subsequently used for the preparation of metal complexes ([ligand] ≈ 0.66 M, [Br$^-$] ≈ 2.6 M).

Preparation of Complexes. [Al(TCTA)]. To 20 mL of the above solution containing the ligand TCTA was added at 60 °C 2.0 g of $AlCl_3·6H_2O$ dissolved in 30 mL of water. The pH of the solution (~0.7) was slowly raised to 7 with 0.5 M NaOH. When the solution cooled, colorless, needle-shaped crystals precipitated, which could be recrystallized from hot water. Anal. Calcd for [$AlC_{12}H_{18}N_3O_6$]: C, 44.04; H, 5.54; N, 12.84. Found: C, 43.8; H, 5.3; N, 12.6.

[VO(TCTAH)]·H$_2$O. To 20 mL of the ligand solution was added a solution of 2.6 g of VO(SO$_4$)·5H$_2$O dissolved in 40 mL of water, and the pH of the resulting solution was adjusted to 1.5. When the solution stood for 2 days at 20 °C, blue-violet crystals precipitated. These were filtered off, washed with ethanol and ether, and air-dried. Anal. Calcd for [$C_{12}H_{19}N_3O_7V$]·H$_2$O: C, 37.31; H, 5.48; N, 10.88; V, 13.19. Found: C, 37.2; H, 5.4; N, 11.0; V, 13.4.

[Cr(TCTA)]. To 20 mL of the ligand solution was added 5.4 g of Cr(ClO$_4$)$_3$·6H$_2$O dissolved in 20 mL of water. The solution was refluxed until a clear red solution was obtained. The pH was adjusted to 7 from time to time by adding 0.5 M NaOH. When the solution

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cooled, red, needle-shaped crystals precipitated, which were recrystallized from hot water (80 °C). Anal. Calcd for $[C_{12}H_{18}N_3O_6Cr]$: C, 40.91; H, 5.15; N, 11.93; Cr, 14.76. Found: C, 40.8; H, 5.1; N, 12.0; Cr, 14.6.

Na[Mn(TCTA)]·6H$_2$O. Ten milliliters of the ligand solution was added to 1.8 g of $Mn(ClO_4)_2\cdot 6H_2O$ dissolved in 5 mL of water. After adjustment of the pH to 7, 40 mL of ethanol was added. In some instances sodium bromide crystallized out within 1 h and was filtered off and discarded. After the resulting solution was kept at room temperature for 3 days, colorless crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Mn]\cdot NaBr\cdot 6H_2O$: C, 24.46; H, 5.13; N, 7.13; Mn, 9.32; Br, 13.56. Found: C, 24.9; H, 4.9; N, 7.2; Mn, 8.6; Br, 12.2. Recrystallization from a hot water–ethanol mixture (1:1) yields the sodium bromide free salt of Na[Mn(TCTA)]·6H$_2$O. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Mn]\cdot 6H_2O$: C, 29.64; N, 8.64; H, 6.22. Found: C, 29.4; N, 8.3; H, 5.5.

[Mn(TCTA)]. A 1.21-g quantity of Na[Mn(TCTA)]·6H$_2$O was dissolved in 7 mL of water, and 0.3 g of $K_2S_2O_8$ was added with stirring. The temperature was raised to 70 °C for 10 min, during which time a deep red solution was obtained. On rapid cooling (0 °C) red, needle-shaped crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. Anal. Calcd for $[C_{12}H_{18}N_3O_6Mn]$: C, 40.57; H, 5.11; N, 11.83. Found: C, 40.4; H, 5.0; N, 11.9.

Na[Fe(TCTA)]·1.5NaClO$_4$·3H$_2$O. A solution of 1.8 g of $Fe(ClO_4)_2\cdot 6H_2O$ in 20 mL of deaerated water was added to 10 mL of the degassed solution of the ligand. The pH was adjusted to 6, and 40 mL of oxygen-free ethanol was added. When the solution was cooled overnight (0 °C), colorless crystals precipitated, which were filtered off under strictly oxygen-free conditions. The complex is very air sensitive and can be stored only under air-free conditions. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Fe]\cdot 1.5NaClO_4\cdot 3H_2O$: C, 23.36; H, 3.92; N, 6.81; Fe, 9.5; ClO$_4$, 24.18. Found: C, 23.7; H, 4.0; N, 6.9; Fe, 8.9; ClO$_4$, 21.5.

[Fe(TCTA)]. To 20 mL of the ligand solution was added at 80 °C 2.0 g of $FeCl_3\cdot 6H_2O$ dissolved in 30 mL of water. The pH of the yellow solution was raised to 7 with 0.5 M NaOH. When the solution cooled, yellow, needle-shaped crystals precipitated, which could be recrystallized from hot water (solubility at 80 °C ~2.5 g of complex in 1 L of H$_2$O). Anal. Calcd for $[C_{12}H_{18}N_3O_6Fe]$: C, 40.47; H, 5.10; N, 11.80; Fe, 15.68. Found: C, 41.0; H, 5.2; N, 11.8; Fe, 15.5.

Na[Co(TCTA)]·2.5H$_2$O. To 20 mL of deaerated TCTA solution (pH ~6.0) was added an oxygen-free solution of 3.6 g of $Co(ClO_4)_2\cdot 6H_2O$ in 10 mL of water. The pH was adjusted to 6 with 0.5 M NaOH, and 140 mL of degassed ethanol was added to the above solution. When the solution cooled overnight, purple crystals precipitated, which were recrystallized from water with ethanol. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Co]\cdot 2.5H_2O$: C, 33.73; H, 5.43; N, 9.84; Co, 13.62. Found: C, 33.7; H, 5.4; N, 9.8; Co, 13.7.

[Co(TCTA)]. To 20 mL of the ligand solution was added at 80 °C 1.4 g of $CoCl_2\cdot 6H_2O$. A 20-mL quantity of 30% H_2O_2 was added dropwise with stirring until a deep red solution was obtained. When the solution cooled, red crystals precipitated, which were recrystallized from hot water. Anal. Calcd for $[C_{12}H_{18}N_3O_6Co]$: C, 40.12; H, 5.05; N, 11.70; Co, 16.41. Found: C, 40.2; H, 5.2; N, 11.7; Co, 16.7.

Na[Ni(TCTA)]·0.5NaClO$_4$·4H$_2$O. A 1.8-g quantity of $Ni(ClO_4)_2\cdot 6H_2O$ dissolved in 10 mL of water was added to 10 mL of the solution containing the ligand TCTA. When the mixture was heated to 60 °C, a deep blue solution was obtained, the pH of which was adjusted to 6. To this solution was added 50 mL of ethanol. The sodium bromide that had precipitated was filtered off. The solution was kept at 0 °C for 2 days, during which time bright blue crystals grew slowly on the surface of the beaker. The crystals were filtered off, washed with ethanol and ether, and air-dried; they could be recrystallized from hot ethanol. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Ni]\cdot 0.5NaClO_4\cdot 4H_2O$: C, 27.97; H, 5.08; N, 8.15; Ni, 11.39; ClO$_4$, 9.65. Found: C, 28.6; H, 5.2; N, 7.9; Ni, 11.7; ClO$_4$, 9.6.

Na[Cu(TCTA)]·2NaBr·8H$_2$O. A 2.0-g quantity of $Cu(ClO_4)_2\cdot 6H_2O$ was dissolved in 10 mL of the ligand solution. After the mixture was heated (50 °C, 10 min) and the pH was adjusted to 7, 40 mL of ethanol was added. When the solution cooled (0 °C, 24 h), bluish green crystals precipitated, which were filtered off, washed with ethanol and ether, and air-dried. These crystals were dissolved in a minimum of water at 25 °C (10 mL), and 10 mL of a concentrated solution of NaBr was added together with 30 mL of ethanol. This solution was kept at 0 °C for 12 h. Needle-shaped blue-green crystals were obtained. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Cu]\cdot 2NaBr\cdot 8H_2O$: C, 19.56; H, 4.65; N, 5.70; Cu, 8.62. Found: C, 19.6; H, 4.7; N, 5.7; Cu, 8.2.

Table I. Crystal Data and Intensity Measurements

	[Cr(TCTA)]	[Fe(TCTA)]	Na[Cu(TCTA)]·2NaBr·8H$_2$O
	Crystal Data		
syst	monoclinic	rhombohedral	triclinic
a, Å	8.825 (9)	13.577 (3)	9.156 (1)
b, Å	13.458 (7)	13.577 (3)	11.679 (3)
c, Å	11.913 (12)	13.264 (4)	14.131 (2)
α, deg	90.0	90.0	104.14 (2)
β, deg	106.09 (10)	90.0	103.81 (1)
γ, deg	90.0	120.0	102.74 (2)
V, Å^3	1359.5	2117	1388
fw	352.3	356.1	736.7
Z	4	6	2
space group	$C_{2h}^5 - P2_1/n$	$C_{3v}^6 - R3c$	$C_i^1 - P\bar{1}$
μ(Mo K$\bar{\alpha}$), cm^{-1}	8.5	11.0	38.2
	Intensity Measurements		
cryst dimens, cm	0.1 × 0.1 × 0.3	0.2 × 0.15 × 0.3	0.2 × 0.3 × 0.4
diffractometer	AED (Siemens)	Syntex R3	Syntex R3
max 2θ, deg	60	60	60
data collcn	θ–2θ	θ–2θ	θ–2θ
std reflctns	2 every 2 h	3 every 2 h	2 every 2 h
obsd data ($I \geqslant 2.5\sigma(I)$)	2272	628	4292
radiation	Mo Kα (λ = 0.710 69 Å)		

A different double salt containing NaClO$_4$ was prepared with use of a concentrated solution of NaClO$_4$ instead of NaBr. Blue-green crystals of Na[Cu(TCTA)]·NaClO$_4$·6H$_2$O were obtained. Anal. Calcd for $Na[C_{12}H_{18}N_3O_6Cu]\cdot NaClO_4\cdot 6H_2O$: C, 23.35; H, 4.90; N, 6.81; Cu, 10.29; ClO$_4$, 16.10. Found: C, 24.0; H, 4.3; N, 7.1; Cu, 9.6; ClO$_4$, 15.6.

Physical Measurements. Cyclic voltammetric experiments were made with a Princeton Applied Research Model 173 potentiostat-galvanostat driven by a Model 175 Universal Programmer. Voltammograms were recorded on a Kipp & Zonen X-Y recorder, Model BD 90. The electrochemical cell used was a conventional three-electrode type with an aqueous Ag/AgCl (saturated KCl) electrode as a reference electrode and a platinum wire as the auxiliary electrode. As working electrode a hanging mercury drop electrode, a glassy carbon, or a platinum-button electrode was used.

The formal reduction potentials were calculated by using the midpoint of the anodic and cathodic peaks of reversible cyclic voltammograms. Formal reduction potentials reported are all vs. the normal hydrogen electrode (NHE).

UV–visible spectra were recorded on a Unicam SP 8-100 at 20 °C (in aqueous solutions).

The magnetic susceptibilities of powdered samples were measured by the Faraday method (Sartorius microbalance, Bruker research magnet B-E10C8 and Bruker B-VT 1000 automatic temperature control) between 100 and 300 K.

The unit cell parameters of [Co(TCTA)], [Mn(TCTA)], and [Al(TCTA)] were determined with use of the Guinier technique (Cu Kα radiation) by least-squares refinements of the respective angular settings of 10 reflections of each complex.

Description of the X-ray Diffraction Studies and Solution of the Structures of 1, 2 and 3. The unit cell parameters were obtained at 23 °C by least-squares refinements of the respective angular setting of 32 reflections of each crystal (Table I). Intensity data were collected on an automated diffractometer, AED (Siemens) for **2**, whereas **1** and **3** were measured on a Syntex R3 diffractometer, and were corrected for Lorentz and polarization effects. An empirical absorption correction has been carried out for **3** whereas no such correction was made for **1** and **2** in view of their small absorption coefficients and crystal dimensions. The scattering factors for neutral atoms were corrected for both the real and the imaginary components of anomalous dispersion. The function minimized during least-squares refinements was $(\sum(|F_o| - |F_c|)^2$.

Table II. Final Atomic Positional ($\times 10^4$) Parameters with Standard Deviations in Parentheses for [$Cr(C_{12}H_{18}N_3O_6)$]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cr	1096 (1)	2482 (1)	3123 (1)	C21	1650 (6)	7497 (6)	3154 (5)
N1	5651 (5)	6473 (4)	2545 (4)	C31	5570 (7)	9225 (5)	1803 (6)
N2	3357 (5)	7318 (4)	3445 (4)	H1A	5796 (6)	5406 (5)	3782 (5)
N3	5502 (5)	8526 (4)	2726 (4)	H1B	6249 (7)	6472 (5)	4290 (5)
O10	2749 (4)	6305 (3)	1150 (3)	H2A	3812 (7)	6214 (5)	4635 (5)
O20	2070 (4)	8354 (3)	1512 (3)	H2B	3200 (7)	5838 (5)	3348 (5)
O30	4663 (4)	7865 (3)	541 (3)	H3A	5148 (7)	7757 (5)	4783 (5)
O11	3139 (5)	4814 (3)	495 (4)	H3B	3595 (7)	8350 (5)	4706 (5)
O21	−227 (5)	8564 (3)	1905 (4)	H4A	5565 (7)	9321 (5)	4221 (5)
O31	5964 (5)	9039 (4)	−96 (4)	H4B	3921 (7)	9342 (5)	3289 (5)
C1	5508 (7)	6095 (5)	3706 (5)	H5A	7871 (7)	8558 (5)	3153 (5)
C2	3878 (7)	6306 (5)	3854 (5)	H5B	7100 (7)	7985 (5)	4061 (5)
C3	4284 (7)	8107 (5)	4271 (5)	H6A	8045 (7)	6661 (5)	3149 (5)
C4	4830 (7)	8942 (5)	3635 (5)	H6B	7248 (6)	7084 (5)	1904 (5)
C5	7061 (6)	8019 (5)	3252 (5)	H11A	5860 (7)	5842 (5)	1060 (5)
C6	7160 (6)	7026 (5)	2684 (5)	H11B	5774 (7)	5038 (5)	1990 (6)
C10	3617 (7)	5553 (5)	1048 (5)	H21A	1123 (6)	6874 (5)	2940 (5)
C20	1090 (6)	8205 (4)	2122 (5)	H21B	1357 (6)	7772 (5)	3806 (5)
C30	5444 (7)	8699 (5)	640 (5)	H31A	4725 (7)	9698 (5)	1665 (6)
C11	5373 (7)	5667 (5)	1659 (6)	H31B	6555 (7)	9570 (5)	1932 (6)

Table III. Final Atomic Positional ($\times 10^4$) Parameters with Standard Deviations in Parentheses for [$Fe(C_{12}H_{18}N_3O_6)$]

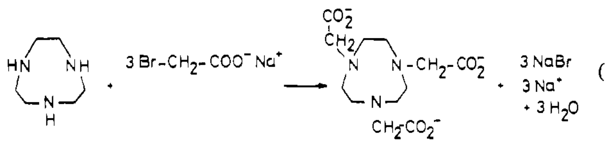
atom	*x*	*y*	*z*
Fe	0	0	0
N1	1233 (2)	104 (2)	−1110 (2)
O1	503 (2)	1392 (2)	792 (2)
O2	178 (2)	2826 (2)	1078 (2)
C1	135 (4)	2085 (3)	545 (3)
C2	−383 (3)	1882 (3)	−505 (3)
C3	1455 (3)	477 (3)	3095 (3)
C4	714 (3)	−1072 (3)	−1540 (3)
H2A	−128 (3)	2598 (3)	836 (3)
H2B	−1194 (3)	1500 (3)	−424 (3)
H3A	1044 (3)	410 (3)	2486 (3)
H3B	2250 (3)	811 (3)	2945 (3)
H4A	1130 (3)	−1107 (3)	−2110 (3)
H4B	688 (3)	−1582 (3)	−1025 (3)

The structures were solved via three-dimensional Patterson syntheses, which yielded the positions of the respective transition metal (Cr, Fe, Cu) and of the bromide ions of 3. Subsequent Fourier syntheses revealed the locations of all remaining non-hydrogen atoms. Refinements were carried out by using anisotropic thermal parameters for all non-hydrogen atoms. At this stage three difference Fourier syntheses revealed the positions of all hydrogen atoms bound to carbon atoms of the ligand TCTA. The refinements were continued with these hydrogens included in calculated, idealized positions (based upon *d*(CH) of 0.97 Å, regular tetrahedral geometry about the carbon atoms, and one isotropic temperature factor, *U*, for all hydrogens). In the case of 3, from a second difference Fourier synthesis the positions of all remaining hydrogen atoms from the water molecules could be located. These were included in the final refinements with one isotropic temperature factor $U = 0.089$. Convergence was reached with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.070$ for 1, 0.027 for 2, and 0.036 for 3. No weighting scheme was applied in the refinements.

The final positional parameters are given in Tables II–IV. Lists of observed and calculated structure factors and thermal parameters (anisotropic for all non-hydrogen atoms and isotropic for hydrogens) are available as supplementary material.

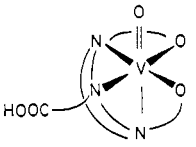
Results and Discussion

Preparation of Complexes. The ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate was prepared by reacting 1,4,7-triazacyclononane with sodium bromoacetate and sodium hydroxide in aqueous solution at 80 °C (eq 1). Attempts to crystallize sodium salts of the ligand from solutions at pH 12, 7, or 5 have failed. It has also not been possible to extract the neutral ligand from aqueous solutions (pH 1.5) with diethyl ether. Therefore, aqueous solutions of the ligand (pH 7) were used in the preparation of complexes containing divalent and trivalent metal ions. Upon addition of aquametal ions (as perchlorate or chloride salts) to such solutions a rapid decrease of pH is observed, indicating the formation of complexes. The pH was raised again (pH 6–7) by adding 0.5 M NaOH. The neutral complexes [M^{III}(TCTA)], with M^{III} = Al, Cr, Mn, Fe, Co, are relatively insoluble in aqueous solution. They precipitate as needle-shaped crystals. With divalent aqua ions such as Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) anionic complexes [M^{II}(TCTA)]$^-$ are formed, which are very soluble in aqueous solution. The corresponding sodium salts can be precipitated with ethanol. In some cases these are crystallized as double salts containing varying amounts of sodium bromide or sodium perchlorate. In general, the anionic complexes are rather difficult to crystallize.



(1)

The reaction of $VOSO_4 \cdot 5H_2O$ with the ligand yields blue crystals of [VO(TCTAH)]$\cdot H_2O$ in which the ligand is only pentadentate, the sixth coordination site being occupied by a terminal oxo ligand. One carboxylato group is not coordinated to the vanadium center but is protonated. The proposed structure



is in agreement with the infrared spectrum (Table V), which indicates the presence of coordinated carboxylate groups, an uncomplexed, protonated –COOH group, and a V=O structural unit (ν(V=O) 950 cm^{-1}).

In all other cases the physical data suggest that the ligand is hexadentate in the solid state.

Electronic Spectra and Magnetic Properties of Complexes. In Table V physical data of TCTA complexes are summarized. The electronic spectra of divalent and trivalent first-row transition-metal complexes are in good agreement with spectra of similar Werner type complexes with these metal ions in a pseudooctahedral environment (facial N_3O_3 donor set). Due to the low symmetry of the $M^{III}N_3O_3$ moieties the molar absorption coefficients of the d–d transition in the visible region, ϵ (L mol^{-1} cm^{-1}), are large (Table V) for [Cr(TCTA)] and [Co(TCTA)].

Table IV. Final Atomic Positional Parameters (×10⁴) with Standard Deviations in Parentheses for $Na[Cu(C_{12}H_{18}N_3O_6)]\cdot 2NaBr\cdot 8H_2O$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu	5795.3 (5)	2176.3 (4)	7380.9 (3)	O_w8	1570 (4)	2037 (3)	5294 (2)
Br1	2378.4 (6)	1800.2 (4)	583.1 (3)	H11A	2282 (4)	883 (3)	8081 (3)
Br2	8299.6 (5)	4815.1 (4)	2066.1 (3)	H11B	2433 (4)	1858 (3)	7491 (3)
Na1	0	0	5000.0	H21A	−2699 (4)	880 (4)	9499 (3)
Na2	5000.0	0	5000.0	H21B	−2685 (4)	2251 (4)	9948 (3)
Na3	7555 (2)	2599 (1)	4112 (1)	H31A	7249 (4)	5595 (3)	8063 (3)
Na4	519 (2)	1521 (1)	3346 (1)	H31B	8024 (4)	4672 (3)	7514 (3)
N1	4524 (3)	1939 (2)	8523 (2)	H1A	4782 (4)	1096 (3)	9517 (3)
N2	−2392 (3)	1844 (2)	8524 (2)	H1B	4839 (4)	300 (3)	8466 (3)
N3	6761 (3)	3958 (2)	8322 (2)	H2A	−878 (5)	835 (3)	8343 (3)
O10	4158 (3)	623 (2)	6485 (2)	H2B	−2657 (5)	63 (3)	7846 (3)
O20	7317 (3)	1525 (2)	6510 (2)	H3A	−357 (4)	3063 (3)	9494 (3)
O30	5009 (3)	3145 (2)	6350 (2)	H3B	672 (4)	3059 (3)	8353 (3)
O11	1779 (3)	−570 (2)	6287 (2)	H4A	8958 (4)	4875 (3)	9262 (3)
O21	−1102 (3)	327 (2)	6478 (2)	H4B	7860 (4)	4150 (3)	9753 (3)
O31	5692 (3)	5000 (2)	6138 (2)	H5A	5835 (4)	4973 (3)	9230 (3)
C10	2938 (4)	361 (3)	6766 (2)	H5B	4664 (4)	4217 (3)	8131 (3)
C20	−1876 (4)	896 (3)	6901 (3)	H6A	3759 (5)	3234 (3)	9222 (3)
C30	5826 (4)	4284 (3)	6645 (3)	H6B	5446 (5)	3184 (3)	9753 (3)
C11	2912 (4)	1289 (3)	7736 (3)	HO11	5390 (50)	−1881 (40)	5921 (35)
C21	−3031 (4)	1553 (4)	9338 (3)	HO12	4970 (51)	−2322 (40)	5002 (35)
C31	7090 (4)	4750 (3)	7686 (3)	HO21	3313 (54)	−2593 (43)	8185 (35)
C1	5170 (4)	1118 (3)	8946 (3)	HO22	4114 (49)	−2396 (39)	7830 (32)
C2	−1898 (5)	837 (3)	7965 (3)	HO31	3244 (47)	−4758 (38)	5359 (31)
C3	−1138 (4)	3032 (3)	8891 (3)	HO32	2623 (51)	−4984 (41)	5954 (34)
C4	8199 (4)	4106 (3)	9156 (3)	HO41	154 (60)	−3666 (49)	6718 (37)
C5	5439 (4)	4182 (3)	8708 (3)	HO42	−619 (62)	−3905 (51)	5861 (41)
C6	4747 (5)	3179 (3)	9125 (3)	HO51	319 (51)	−3620 (41)	3726 (32)
O_w1	4873 (3)	−1839 (2)	5531 (2)	HO52	1456 (49)	−2507 (38)	3934 (32)
O_w2	3748 (5)	−2137 (3)	7712 (3)	HO61	103 (56)	1365 (45)	1234 (37)
O_w3	2534 (3)	−4773 (3)	5558 (2)	HO62	−1157 (69)	684 (60)	1151 (46)
O_w4	0 (4)	−3473 (3)	6220 (2)	HO71	3177 (50)	3112 (41)	3305 (34)
O_w5	807 (3)	−3060 (2)	4193 (2)	HO72	2816 (50)	2324 (40)	2365 (34)
O_w6	−649 (5)	1047 (4)	1518 (3)	HO81	2636 (54)	2423 (44)	5614 (36)
O_w7	2915 (3)	2458 (2)	3089 (2)	HO82	1169 (64)	2344 (52)	5547 (42)

Table V. Physical Data of Complexes (UV-Visible, Infrared, Magnetic Moment)

complex	λ_{max}, nm (ϵ, L mol⁻¹ cm⁻¹)	color	ν(C=O), cm⁻¹	μ_{eff}, μ_B
[OV(TCTA)]⁻	335 sh, 573 (1.2 × 10²), 775 (60.0)	blue-violet	1590, 1620 1690, 1720	1.6
[Cr(TCTA)]	388 (2.2 × 10²), 512 (3.4 × 10²)	red	1660	3.6
[Mn(TCTA)]	471 (7.2 × 10²), 481 sh (7.0 × 10²)	red	1700, 1650	4.95
[Mn(TCTA)]⁻		colorless	1580	5.7
[Fe(TCTA)]	257 (1.2 × 10⁴)	yellow	1660	5.7
[Fe(TCTA)]⁻		colorless	1600	5.6
[Co(TCTA)]	372 (1.94 × 10²), 511 (3.3 × 10²)	red	1650	diamagnetic
[Co(TCTA)]⁻	365 (5.2), 500 (20.6), 660 (5.1)	purple	1590	4.4
[Ni(TCTA)]⁻	355 (18.2), 557 (13.1), 805 sh (16.9), 924 (33.6)	blue	1580, 1600	2.8
[Cu(TCTA)]⁻	750 (72.2)	blue-green	1590, 1630	1.6
[Al(TCTA)]		colorless	1685, 1705	diamagnetic

Absorption spectra of all complexes in aqueous solution are stable for at least 24 h at 25 °C and are independent of pH of the solutions in the range 1–10. This is taken as further evidence that—with the exception of [VO(TCTA)]·H_2O—the ligand is invariably hexadentate and the metal ions are all six-coordinate. This stereochemical stability is in contrast to the structural diversity of analogous complexes of EDTA which in some cases are known to be seven-coordinate, e.g., $[Mn^{II}(EDTA)H_2O]^{2-}$ [7] and $[Fe^{II}(EDTA)H_2O]^-$,[8] or six-coordinate but with a pentadentate EDTA ligand and an additional aquo ligand, $[Cr(EDTA)H_2O]^-$.[9]

The magnetic moments between 100 and 300 K have been measured (Table V). The Curie–Weiss law is obeyed in all cases; the moments are close to the spin-only values. $[M^{II}(TCTA)]^-$ species with M = Fe^{II}, Co^{II}, Mn^{II} and $[M^{III}(TCTA)]$ complexes with M = Fe^{III}, Mn^{III} are found to be high-spin complexes; the $[Ni(TCTA)]^-$ anion shows the moment of 2.8 μ_B as is expected for nickel(II) in an octahedral ligand field.

Table VI. Formal Reduction Potentials of $[M(TCTA)]/[M(TCTA)]^-$ Couples at 20 °C vs. NHE

M	*E*°, V	Δ*E*, mV[c]	M	*E*°, V	Δ*E*, mV[c]
Cr[a]	−1.17 (1)	85	Co[a]	0.00 (1)	60
Mn[b]	+0.80 (1)	95	Ni[b]	+1.16 (1)	80
Fe[a]	+0.195 (10)	60			

[a] Aqueous solution, 0.05 M $LiClO_4$. [b] Aqueous solution, 0.05 M KCl. [c] Separation between the anodic and cathodic peaks of the cyclic voltammogram at a scan rate of 10 mV/s.

Formal Potentials of $[M(TCTA)]^{0/-}$ Couples. The formal electrode potentials were measured in aqueous solution ($LiClO_4$ or KCl as supporting electrolyte) at pH 7 and 20 °C for the $[M(TCTA)]^{0/-}$ couples:

$$[M^{III}(TCTA)] + e^- \rightleftarrows [M^{II}(TCTA)]^-$$
$$M = Cr, Mn, Fe, Ni, Co$$

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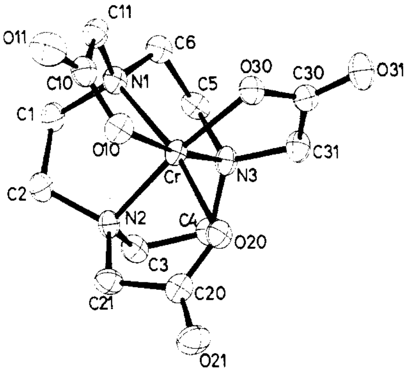
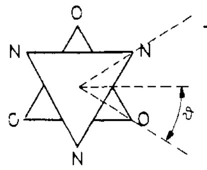


Figure 1. ORTEP view (50% probability ellipsoids) of the non-hydrogen atoms of [Cr(TCTA)].

Chart I



	ϑ
[Fe(TCTA)]	12.6(2)°
[Cr(TCTA)]	24.5(2)°
$[Cu(TCTA)]^-$	13.3(2)°
$[Ni(TCTA)]^-$	22.5(9)°
octahedron	30°
prisma	0°

For the TCTA complexes of Cr, Mn, Fe, Co, and Ni a single reversible cyclic voltammogram was observed at a scan rate of 10 mV/s. The separation of anodic and cathodic peaks (Table VI) and the peak height ratios of approximately unity of the respective complexes indicate reversible one-electron systems in each case.

Details of the stable $[Ni^{III}(TCTA)]$ complex, which has also been generated by the pulse radiolytic technique, will be reported elsewhere. It was found that this Ni(III) species is stable in deaerated aqueous solution for at least 24 h at 25 °C.[10] $[Cr^{II}(TCTA)]^-$ is a very strong reductant—very similar to the case for the analogous $[Cr^{II}(EDTA)]$ complexes[11] ($E°$ = −1.0 V)—whereas $[Mn^{III}(TCTA)]$ is a strong oxidant, which again is paralleled by the corresponding $[Mn^{III}(EDTA)]$ complex[12] ($E°$ = +0.81 V). For $[Fe^{III}(EDTA)]/[Fe^{II}(EDTA)]$ a reduction potential of +0.11 V has been determined,[12] which is also in line with a potential of +0.195 V for the $[Fe^{III}(TCTA)]/[Fe^{II}(TCTA)]^-$ couple.

Interestingly, the couple $[Co^{III}(TCTA)]/[Co^{II}(TCTA)]^-$ exhibits also a reversible cyclic voltammogram ($E°$ = 0.00 V) in contrast to the $[Co^{III}(EDTA)]/[Co^{II}(EDTA)]$ couple, for which a reduction potential of +0.36 V has been determined.[20] The $[Co^{III}(EDTA)]$ complex is a much stronger oxidant. This behavior may be taken as further indication that the [Co(TCTA)] species are six-coordinate in both oxidation states whereas the $[Co^{II}EDTA]$ complex is thought to have a pentadentate ligand and a coordinated water molecule.[20]

Table VII. Bond Distances (Å) of [Cr(TCTA)], [Fe(TCTA)], and $Na[Cu(TCTA)]\cdot 2NaBr\cdot 8H_2O$

[Cr(TCTA)]		[Fe(TCTA)]		$[Cu(TCTA)]^-$	
Cr–N1	2.045 (5)	Fe–N1	2.181 (3)	Cu–N1	2.115 (3)
Cr–N2	2.072 (5)			Cu–N2	2.197 (3)
Cr–N3	2.051 (5)			Cu–N3	2.039 (2)
Cr–O10	1.954 (4)	Fe–O1	1.962 (2)	Cu–O10	1.978 (2)
Cr–O20	1.950 (4)			Cu–O20	2.205 (3)
Cr–O30	1.964 (4)			Cu–O30	2.141 (3)
C10–O10	1.296 (7)	C1–O1	1.309 (6)	C10–O10	1.273 (4)
C10–O11	1.204 (7)	C1–O2	1.207 (6)	C10–O11	1.247 (3)
C10–C11	1.529 (8)	C1–C2	1.521 (6)	C10–C11	1.535 (5)
C20–O20	1.291 (8)			C20–O20	1.278 (5)
C20–O21	1.219 (7)			C20–O21	1.232 (5)
C20–C21	1.529 (8)			C20–C2	1.525 (6)
C30–O30	1.305 (8)			C30–O30	1.282 (4)
C30–O31	1.191 (8)			C30–O31	1.235 (5)
C30–C31	1.537 (9)			C30–C31	1.522 (4)
N1–C11	1.489 (8)	N1–C2	1.490 (6)	N1–C11	1.469 (4)
N1–C1	1.516 (8)	N1–C3	1.501 (4)	N1–C1	1.484 (5)
N1–C6	1.496 (7)	N1–C4	1.497 (4)	N1–C6	1.481 (4)
N2–C21	1.470 (7)			N2–C2	1.471 (5)
N2–C2	1.477 (8)			N2–C21	1.485 (5)
N2–C3	1.526 (7)			N2–C3	1.475 (4)
N3–C4	1.485 (8)			N3–C4	1.487 (4)
N3–C5	1.510 (7)			N3–C5	1.488 (4)
N3–C31	1.465 (8)			N3–C31	1.472 (5)
C1–C2	1.524 (9)	C3–C4	1.509 (5)	C1–C21	1.529 (5)
C3–C4	1.508 (9)			C3–C4	1.516 (6)
C5–C6	1.512 (9)			C5–C6	1.520 (6)

Table VIII. Distances (Å) within the Coordinated Ligand TCTA of [Cr(TCTA)], [Fe(TCTA)], and $Na[Cu(TCTA)]\cdot 2NaBr\cdot 8H_2O$

Cr		Fe		Cu	
		Bonding Distances			
N1–C11	1.489 (8)	N1–C2	1.490 (5)	N1–C11	1.469 (4)
N2–C21	1.470 (7)			N2–C2	1.471 (5)
N3–C31	1.465 (8)	N1–C4	1.497 (4)	N3–C31	1.472 (5)
N1–C6	1.496 (7)			N1–C6	1.481 (4)
N2–C2	1.477 (8)	N1–C3	1.501 (4)	N2–C21	1.485 (5)
N3–C4	1.485 (8)			N3–C4	1.487 (4)
N1–C1	1.516 (8)	O1–C1	1.309 (6)	N1–C1	1.484 (5)
N2–C3	1.526 (7)			N2–C3	1.475 (4)
N3–C5	1.510 (7)	O2–C2	1.207 (6)	N2–C5	1.488 (5)
O10–C10	1.296 (7)			O10–C10	1.273 (4)
O20–C20	1.291 (8)	C1–C2	1.521 (6)	O20–C20	1.278 (5)
O30–C30	1.305 (8)			O30–C30	1.282 (4)
O11–C10	1.204 (7)	C3–C4	1.509 (5)	O11–C10	1.247 (3)
O21–C20	1.219 (7)			O21–C20	1.232 (5)
O31–C30	1.191 (8)			O31–C30	1.235 (5)
C10–C11	1.529 (8)			C10–C11	1.535 (5)
C20–C21	1.529 (8)			C20–C2	1.525 (6)
C30–C31	1.537 (9)			C30–C31	1.522 (4)
C1–C2	1.524 (9)			C1–C21	1.529 (5)
C3–C4	1.508 (9)			C3–C4	1.516 (6)
C5–C6	1.512 (9)			C6–C6	1.520 (6)
		Nonbonding Distances			
N1-N2	2.783	N1-N1	2.786	N1-N2	2.849
N1-N3	2.777			N1-N3	2.883
N2-N3	2.803			N2-N3	2.803
O10–O20	2.868	O1–O1	2.870	O10–O20	2.840
O20–O30	2.908			O20–O30	3.137
O10–O30	2.910			O10–O30	2.941

Structure of [Cr(TCTA)]. The structure consists of monomeric, neutral molecules of [Cr(TCTA)] (Figure 1). Each chromium ion is coordinated by six atoms, i.e. three nitrogens and three oxygens occupying facial positions, respectively, of a distorted octahedron. The degree of distortion from the regular octahedral arrangement of the N_3O_3 donor set may be expressed by the twist angle, ϑ, defined in Chart I. ϑ is 0° for a prismatic and 30° for an octahedral arrangement. The observed angle of 24.5° indicates the propensity of Cr(III)

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Table IX. Selected Bond Angles (Deg) of [Cr(TCTA)], [Fe(TCTA)], and $Na[Cu(TCTA)]\cdot 2NaBr\cdot 8H_2O$[a]

[Cr(TCTA)]		[Fe(TCTA)]		[Cu(TCTA)]$^-$	
N2-Cr-N1	85.1 (2)	N1-Fe-N1'	79.4 (1)	N2-Cu-N1	81.7 (1)
N3-Cr-N1	85.4 (2)			N3-Cu-N1	85.5 (1)
N3-Cr-N2	85.8 (2)			N3-Cu-N2	82.8 (1)
O10-Cr-N1	83.1 (2)	O1-Fe-N1'	78.4 (1)	O10-Cu-N1	82.2 (1)
O10-Cr-N2	95.3 (2)	O1'-Fe-N1'	114.4 (1)	O10-Cu-N2	111.8 (1)
O10-Cr-N3	168.3 (2)	O1-Fe-N1'''	150.9 (1)	O10-Cu-N3	159.1 (1)
O20-Cr-N1	167.9 (2)			O20-Cu-N1	148.4 (1)
O20-Cr-N2	83.1 (2)			O20-Cu-N2	76.3 (1)
O20-Cr-N3	96.5 (2)			O20-Cu-N3	113.4 (1)
O20-Cr-O10	95.1 (2)	O1-Fe-O1'	94.0 (1)	O20-Cu-O10	85.3 (1)
O30-Cr-N1	95.8 (2)			O30-Cu-N1	116.6 (1)
O30-Cr-N2	168.7 (2)			O30-Cu-N2	153.1 (1)
O30-Cr-N3	83.1 (2)			O30-Cu-N3	79.4 (1)
O30-Cr-O10	96.0 (2)			O30-Cu-O10	91.1 (1)
O30-Cr-O20	96.2 (2)			O30-Cu-O20	92.4 (1)

[a] Only angles within the MN_3O_3 polyhedron are given.

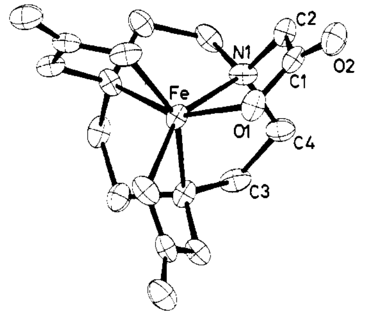

Figure 2. ORTEP view (50% probability ellipsoids) of the non-hydrogen atoms of [Fe(TCTA)].

centers for an octahedral environment.

Bond distances within the CrN_3O_6 polyhedron are given in Table VII; bond distances within the TCTA ligand are summarized in Table VIII; bond angles of the CrN_3O_3 polyhedron are listed in Table IX.

The geometry of the coordinated 1,4,7-triazacyclononane fragment ($C_6H_{12}N_3$) of TCTA is very similar to that observed in the trinuclear complex $[Cr_3([9]aneN_3)_3(OH)_5I_5]\cdot 5H_2O$[14] containing the ligand 1,4,7-triazacyclononane or $[Cr_2([9]\text{-}aneN_3)_2(OH)_2CO_3]I_2\cdot H_2O$.[17] This fragment behaves as a rather rigid structural unit as has been reported for the acetate-free tridentate ligand 1,4,7-triazacyclononane.[14-17]

Structure of [Fe(TCTA)]. The structure consists also of monomeric, neutral molecules of [Fe(TCTA)] (Figure 2), but contrary to the case for [Cr(TCTA)], which crystallizes in a monoclinic geometry, [Fe(TCTA)] crystallizes in a rhombohedral geometry. The molecules have crystallographically imposed C_3 symmetry—the iron atoms lie on threefold axes. The central iron ions are six-coordinated to three nitrogens and three oxygens of the hexadentate ligand. In contrast to the case for the [Cr(TCTA)] complex a twist angle, ϑ, of only 12.6° (Scheme I) indicates a distorted-prismatic environment rather than octahedral—generated by the N_3O_3 ligand donors. [Fe(TCTA)] is a high-spin complex (d^5), and therefore, no electronic preference of an octahedral environment over any other geometry is to be expected in terms of simple ligand field stabilization energy arguments. The same arguments favor an octahedral geometry over the prismatic by $-1.3Dq$ for a d^3 configuration[18] (Cr(III)). Therefore, we propose that the steric requirements of the ligand alone govern the stereochemistry of the complex [Fe(TCTA)].

Bond distances and angles within the 1,4,7-triazanonane fragment of the ligand TCTA in Fe^{III}(TCTA) are very similar to those observed in [Cr(TCTA)], indicating its rigid nature (Table VIII). Comparison of the nonbonding distances of the three nitrogens—forming an equilateral triangle—and three coordinated oxygens of the ligand in [Cr(TCTA)] and [Fe(TCTA)] respectively shows them to be very similar despite the differences of their overall structures.

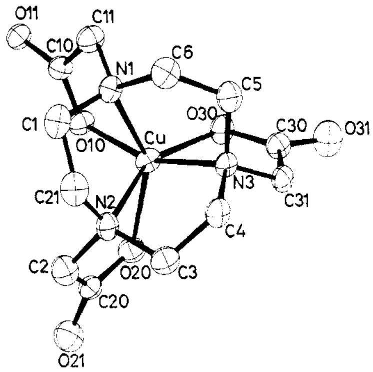

Figure 3. ORTEP view (50% probability ellipsoids) of the non-hydrogen atoms of the anion [Cu(TCTA)]$^-$.

Structure of $Na[Cu(TCTA)]\cdot 2NaBr\cdot 8H_2O$. The structure consists of the complex anion [Cu(TCTA)]$^-$, sodium cations, uncomplexed bromide anions, and molecules of water of crystallization. The structure of the anion, [Cu(TCTA)]$^-$, is shown in Figure 3. The copper(II) ions are six-coordinated by three nitrogens and three oxygens of the chelate ligand. A twist angle, ϑ, of 13.3° indicates a distorted-pseudo-prismatic geometry of the CuN_3O_3 polyhedron. Simple ligand field stabilization energy arguments[18] show that for a d^9 electronic configuration an octahedral geometry is favored by only $-0.5Dq$ over a prismatic arrangement. We feel that in this case the steric requirements of the ligand override this small difference in LFSE. It is of interest that for the [Ni(TCTA)]$^-$ anion (Ni(II); d^8 high-spin configuration) a twist angle of 23° is found,[19] indicating a distorted-octahedral geometry. Here it can be shown that the $-1.3Dq$ of LFSE is in favor of the octahedral rather than the prismatic arrangement.

Bond distances (Table VIII) within the 1,4,7-triazacyclononane fragment of coordinated TCTA are very close to those reported for $[([9]aneN_3)CuBr_2]$,[15] stressing again the rigidity of this structural unit. The Cu–N and Cu–O bond distances vary considerably (Table VII)—the CuN_3O_3 polyhedron is highly distorted (Table IX).

The sodium cations are surrounded by six oxygens, respectively, from carboxylate groups of the coordinated ligand and from water of crystallization. Bond distances of NaO_6 polyhedra are summarized in Table X. Figure 4 shows a section of the crystalline arrangement emphasizing the geometries of the sodium cations. The complex anion [Cu(TCTA)]$^-$ may be divided into a hydrophobic part consisting of the 1,4,7-triazacyclononane fragment and a more hydrophilic

Table X. Bond Distances (Å) of the NaO_6 Octahedron of $Na[Cu(TCTA)]\cdot 2NaBr\cdot 8H_2O$ and Short Hydrogen Bonds (<3.0 Å)

Na1–O_w8	2.371 (3)	Na2–O_w1	2.431 (3)
Na1–O11	2.462 (2)	Na2–O10	2.409 (2)
Na1–O21	2.512 (3)	Na2–O20	2.557 (3)
Na3–O_w1	2.422 (3)	Na4–O_w4	2.395 (4)
Na3–O_w2	2.435 (4)	Na4–O_w6	2.418 (4)
Na3–O_w3	2.490 (4)	Na4–O_w7	2.379 (3)
Na3–O_w4	2.450 (4)	Na4–O_w8	2.556 (3)
Na3–O_w5	2.361 (3)	Na4–O11	2.388 (3)
Na3–O11	2.540 (3)	Na4–O21	2.390 (3)
O_w1–O30	2.763 (4)	O_w7–O31	2.777 (3)
O_w7–O_w1	2.807 (3)	O_w4–O_w3	2.916 (3)
O_w5–O20	2.735 (3)	O_w8–O30	2.972 (3)
O_w8–O_w5	2.857 (3)		

Table XI. Unit Cell Parameters for Isotypic Complexes [Cr(TCTA)], [Mn(TCTA)], [Co(TCTA)], and [Al(TCTA)], Space Group $C_{2h}^5 - P2_1/n$

	Cr	Mn	Co	Al
a, Å	8.825 (9)	8.94 (1)	8.741 (10)	8.82 (1)
b, Å	13.458 (7)	13.88 (1)	13.43 (1)	13.50 (1)
c, Å	11.913 (12)	11.72 (1)	11.84 (1)	12.00 (1)
β, deg	106.09 (10)	104.3 (1)	106.4 (1)	106.3 (1)
V, Å^3	1359.5	1408.6	1332.9	1372.4

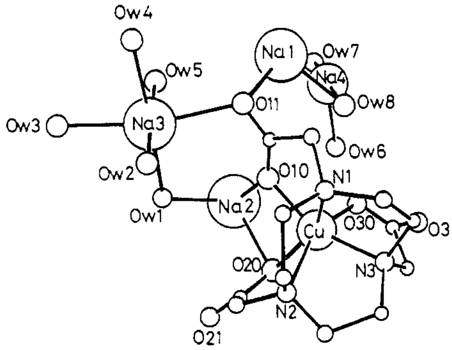

Figure 4. Section of the crystalline arrangement of $Na[Cu(TCTA)]\cdot 2NaBr\cdot 8H_2O$ (derived from an ORTEP plot).

counterpart comprising six oxygens of three coordinated carboxylate groups (these lie roughly on one plane). Only the oxygens O30 and O31 of one carboxylate group are not connected with sodium cations; instead they are bound to two molecules of water of crystallization via two short hydrogen bonds (O_w8···O30 and O_w7···O31, Table X). The terminal carbonyl oxygen (O11) is coordinated to *three* sodium cations (Na1, Na3, Na4) attaining a coordination number 4.

There are three bridging water molecules (O_w1, O_w4, and O_w8) between two sodium cations, respectively.

Structures of [Mn(TCTA)], [Co(TCTA)], and [Al(TCTA)]. An X-ray study of powdered samples of [Mn(TCTA)], [Co(TCTA)], and [Al(TCTA)] using the Guinier technique revealed that these complexes crystallize isotypically with [Cr(TCTA)], i.e. monoclinic in the space group C_{2h}^5. The respective unit cell parameters are all very similar (Table XI); pronounced deviations are found for the [Mn(TCTA)] complex. It is reasonable to assume that for these complexes the distorted-octahedral geometry of the N_3O_3 donor set of TCTA prevails and that a distorted-prismatic environment leads to a different rhombohedral space group as has been established for [Fe(TCTA)].

The infrared spectrum of [Mn(TCTA)] indicates the presence of two differently coordinated carboxylate groups with two different Mn–O distances. This may be due to Jahn–Teller effects frequently observed for high-spin manganese(III) complexes. The same behavior has been described for the $[Mn^{III}(EDTA)]^-$ anion.[12]

Summary. We have shown that the hexadentate ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate forms very stable complexes with many first-row transition metals in the oxidation states +2 and +3. The coordination number was invariably found to be 6, contrasting the more diverse ligating behavior of EDTA. The geometry of the N_3O_3 donor set of TCTA appears to be more or less trigonal prismatic rather than pseudooctahedral in cases where there is no ligand field stabilization energy (Fe^{3+}, d^5 high spin) or where the octahedral geometry is favored by only $-0.5Dq$ (Cu^{2+}, d^9). This indicates that the steric requirements of the ligand are best met by a trigonal-prismatic coordination. Octahedral geometry is favored over the prismatic geometry by $-1.3Dq$ for TCTA complexes of Cr(III) (d^3) and Ni(II) (d^8). Twist angles, ϑ, of 24.5 and 23° are in agreement with these simple ligand field energy arguments.[21] The formal reduction potentials of the couples $[M(TCTA)]^{0/-}$ span a wide range. Therefore, the complexes are ideally suited for the study of outer-sphere electron-transfer reactions with a small or a large driving force. Kinetic measurements are in progress and will be reported.

Acknowledgment. We gratefully acknowledge financial support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. O. Ermer for calculating the twist angles, ϑ, and Herrn Walz for his help with the preparation of the ligand.

Note Added in Proof. After the present research had been completed and had been accepted for publication the work of Takahashi and Takamoto (Takahashi, M.; Takamoto, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3413) and of Arishima, Hamada, and Takamoto (Arishima, T.; Hamada, K.; Takamoto, S. *Nippon Kagaku Kaishi* **1973**, 1119) was brought to our attention. These authors describe the preparation of the ligand and the complexes [Co(TCTA)], [Cr(TCTA)], and [Fe(TCTA)]. In addition, some stability constants of divalent transition metals with the ligand were determined. Where their results and the present work overlap good agreement is observed.

Registry No. **1**, 65532-07-2; **2**, 65532-04-9; **3**, 82980-35-6; Al(TCTA), 82980-26-5; VO(TCTAH), 82995-05-9; Na[Mn(TCTA)]·NaBr, 82980-27-6; Na[Mn(TCTA)], 82980-28-7; Mn(TCTA), 82980-29-8; $Na[Fe(TCTA)]\cdot 1.5NaClO_4$, 82980-31-2; Na[Co(TCTA)], 82980-32-3; Co(TCTA), 65532-10-7; $Na[Ni(TCTA)]\cdot 0.5NaClO_4$, 82980-34-5; $Na[Cu(TCTA)]\cdot NaClO_4$, 82980-37-8.

Supplementary Material Available: Listings of thermal parameters and observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

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(21) As a reviewer has pointed out to us, the ionic radii of all the ions involved are somewhat different. Consequently, the M–N and M–O bond lengths vary. This may produce varying degrees of strain within the ligand which may be minimized by a twist into either a trigonal-prismatic or a more octahedral geometry. The present data do not provide sufficient information if this effect is in the same direction as the LFT results or opposed to them. Nevertheless, to a first approximation the simple LFT arguments correctly reflect the trend of the observed twist angles, ϑ.