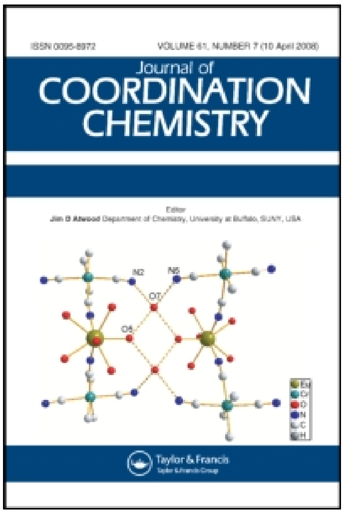

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Chromium(III) Complexes with Quadridentate Amines. Crystal Structure of [*cis-β*-Cr(trien)(C_2O_4)] Cl·2H_2O (I) and [Cr_2(μ-OH)$_2$(μ-tren)$_2$] Br_4·2H_2O (II)

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CHROMIUM(III) COMPLEXES WITH QUADRIDENTATE AMINES. CRYSTAL STRUCTURE OF [*CIS*-β-Cr(TRIEN)(C_2O_4)] $Cl \cdot 2H_2O$ (I) and [$Cr_2(\mu$-$OH)_2(\mu$-TREN$)_2$] $Br_4 \cdot 2H_2O$ (II)

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[*cis*-β-Cr(trien) C_2O_4)] $Cl \cdot 2H_2O$ (**I**) ($CrC_8H_{22}N_4O_6Cl$) crystallizes at 22°C, from deionized water solution as a racemate in space group Pn (No. 7). Lattice constants are: $a = 7.193(2)$, $b = 9.1545(12)$, $c = 11.469(2)$ Å; $\beta = 100.994(13)°$; $V = 741.3(3)$ Å^3 and $D_{calc} = 1.603\,g\,cm^{-3}$ (MW = 357.75, $Z = 2$). A total of 2251 data were collected, using MoKα radiation ($\lambda = 0.71703$ Å), over the range $4 \leq 2\theta \leq 60°$; of these, 1441 (independent and with $I \geq 2\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 9.81\,cm^{-1}$) and the transmission coefficients ranged from 0.8676 to 0.9942. The final $R(F)$ and $R_w(F)$ residuals were 0.0338 and 0.0764, respectively. The cations of (**II**) exist in the lattice as enantiomeric pairs. [$Cr_2(\mu$-$OH)_2(\mu$-tren$)_2]Br_4 \cdot 2H_2O$ (**II**) ($Cr_2C_{12}H_{42}N_8O_4Br_4$) crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with $a = 10.835(2)$ Å, $b = 7.859(3)$ Å, $c = 16.397(2)$ Å, $\beta = 105.45(2)°$, $V = 1345.7(5)$ Å^3 and $D_{calc} = 1.940\,g\,cm^{-3}$ (MW = 786.18, $Z = 4$). A total of 2467 data were collected, using MoKα radiation ($\lambda = 0.71703$ Å), over the range $4 \leq 2\theta \leq 50°$; of these, 1450 (independent and with $I \geq 2\sigma(I)$) were used in the structural analysis. Data were corrected for absorption ($\mu = 67.79\,cm^{-1}$) and the transmission coefficients ranged from 0.5589 to 0.9949. The final $R(F)$ and $R_w(F)$ residuals were 0.0481 and 0.1408, respectively for 2385 observed reflections with ($I \geq 2\sigma(I)$). In the complex cation, the two Cr(III) centers are in a distorted octahedral environment and are bridged by two hydroxide groups and two ethylamine arms, one from each tren ligand, which spans over the binuclear core. Within the bridging moiety, the Cr$\cdots$Cr separation is 3.005(2) Å, the ∠Cr–OH–Cr = 101.3(2)° and ∠O–Cr–O = 78.7(2)°, while the average Cr–N bond distance *trans* to the hydroxo groups (2.085(6) Å) is shorter than the corresponding *cis* Cr–N distance (2.104(5) Å).

Keywords: Chromium complexes; Amines; Oxalato; Hydroxo; Dinuclear complexes; Crystallization; Racemates; Conglomerates

INTRODUCTION

Hereafter, trien = 1,8-diamino-3,6-diazaoctane; tren = tris(2-aminoethyl)amine; trpn = tris(3-aminopropyl)amine, 332 = *N*,*N*-bis(3-aminopropyl)-1,2-diaminoethane, en = 1,2-diaminoethane and TTHA = triethylenetetraaminehexaacetic acid.

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The crystallization behavior of cobalt(III)-amine-oxalato complexes was the subject of extensive studies [1–6]. This was attributed to the ease of synthesizing the cobalt(III) complexes and to their tendency to crystallize in monomeric forms at ambient temperature. On the other hand, the corresponding chromium(III) complexes were little studied [7–13], probably due to their ability to form hydroxo and/or binuclear species [14–17], as reactions are sometimes associated with compositional changes in solutions [18].

In the course of studying the factors that might affect the crystallization process by which a racemic metal–amine complex crystallizes as a conglomerate, a number of factors were investigated. These include charge compensation of the counter anions, hydrogen bonding and nature of the coordinated amines as well as the other coordinated ligands [19]. Also, the nature of the central metal ion appears to have an influence in selecting the crystallization pathway of the complex. It has been known for sometime that $[Co(en)_2(ox)]X$ ($X = Cl$, Br) [10–12,20], $[Cr(en)_2(ox)]X$ ($X = Cl$, Br) [11,12], and $[Rh(en)_2(ox)]Br$ [10] crystallize as conglomerates. On the other hand, the pair of compounds $[NH_4][Cr(en)_2(ox)]Cl_2 \cdot H_2O$ [13] and $[OH_3][Co(en)_2(ox)]Cl_2 \cdot H_2O$ [21] were found to crystallize as racemates, and this was attributed to the hydrogen bond between the onium cation and the oxalato oxygens, which in turn prevents the formation of the helical strings which are always observed upon conglomerate crystallization [1–5,13,18,21,22]. Thus, to understand how the central metal ion might affect the crystallization process, we decided to synthesize a series of chromium(III)-amine-oxalato and nitro compounds and compare them with the corresponding cobalt(III) analogues. This manuscript reports the synthesis of the Cr(III) complex, [*cis*-β-Cr(trien)(C_2O_4)]Cl $\cdot$ $2H_2O$ (**I**) compared to [*cis*-β-Co(trien)(C_2O_4)]Cl $\cdot$ $3H_2O$ and [*cis*-β-Co(trien)(C_2O_4)]ClO_4, which are known to crystallize as racemates [6].

Also, in an attempt to synthesize $[Cr(tren)(NO_2)_2]X$ ($X = Cl$, Br) complexes for comparison to the crystallization behavior of cobalt(III) analogues [22], a binuclear complex, $[Cr_2(\mu\text{-}OH)_2(\mu\text{-}tren)_2]Br_4 \cdot 2H_2O$ (**II**) was obtained. A number of complexes in which the metal centers are bridged by hydroxo, oxo, carboxylato, and acetato groups have been reported to serve as models for a variety of biological reactions [23–27]. Numerous examples of binuclear Fe(III) [28,29], Cu(II) [30–35] and Ni(II) [36,37] complexes linked by hydroxo, oxo, carboxylato and acetato groups have been structurally characterized; chromium (III) complexes [14–16], especially when the two chromium centers are bridged at the same time with an aliphatic chain amine, are a part of this class of compounds. In fact a few examples of this type of complex have been structurally characterized [16,17]. Similar amine bindings were also found in the di-(μ-oxo) bridged Mn(III)–Mn(IV) complex $[Mn_2(\mu\text{-}O)_2(\mu\text{-}tren)_2](CF_3SO_3)_3$ [38]. The increased interest in these systems as models for biological reactions encourages us to report the crystal and molecular structure of complex **II**.

EXPERIMENTAL

Materials

Reagent grade chemicals were used throughout this work unless otherwise mentioned. Elemental analyses were performed at Galbraith Laboratories, Knoxvile, TN USA.

Preparation of the Complexes

[Cr(trien)Cl$_2$]Cl To a well-stirred DMSO solution (30 mL) of chlorodimethylsulfoxidechromium(III) [39] (0.05 mol), heated at 150°C, trien (7.5 g, 0.05 mol) was added drop by drop. After the addition, the temperature of the reaction mixture was gradually raised to 190°C and stirring was continued at this temperature for 20 min; then, the reaction mixture was cooled to room temperature. The violet precipitate, which separated out, was collected by filtration, washed with acetone, ether and air-dried. The crude solid was recrystallized by dissolving it into 40 mL of 6 M HCl at 50°C. The product was filtered and washed with an enormous amount of MeOH until the washings became clear (yield: 19 g, 62%).

[Cr(tren)Cl$_2$]Cl This complex was prepared by dropwise addition of tren (0.05 mol) to a well stirred hot solution of cholorodimethylsulfoxidechromium(III) [39] (0.05 mol) in DMSO (30 mL). The solution was heated at 180–190°C for 15 min, during which a violet precipitate commenced to precipitate. Heating and stirring was continued for another 15 min, and the mixture was then allowed to cool to room temperature. The precipitate was collected by filtration, washed with absolute ethanol and air-dried (yield; 7.5 g, 50%).

[cis-β-Cr(trien)C$_2$O$_4$]Cl · 2H$_2$O (**I**) A solution of [Cr(trien)Cl$_2$]Cl (1.52 g, 5 mmol) dissolved in 60 mL of water, was heated on a steam-bath for 15 min. To this solution sodium oxalate (70 mg, 5 mmol) was added and heating was continued until the volume was reduced to *ca.* 30 mL. The product was then allowed to crystallize at room temperature. After two weeks, red crystals suitable for structure determination separated out. These were collected by filtration, washed with ethanol, ether and air-dried (yield: 0.65 g, 36%). No attempts were made to improve the yield. Calcd. for $CrC_8H_{22}N_4O_6$ (Cl%): C, 26.86; H, 6.20; N, 15.66. Found: C, 26.63; H, 6.36; N, 15.50.

[Cr$_2$(μ-OH)$_2$(μ-tren)$_2$]Br · H$_2$O (**II**) To [Cr(tren)Cl$_2$]Cl (0.6 g, 2 mmol) dissolved in water (15 mL), an aqueous solution of NaNO$_2$ (0.3 g, 4.3 mmol in 5 mL water) was added and the resulting mixture heated on a steam-bath for 15 min. The solution was then allowed to crystallize at room temperature. After two weeks, brown-orange crystals separated, were collected by filtration, washed with absolute ethanol and air dried. The yield of the product was about 5%. Calcd. for $Cr_2C_{12}H_{42}N_8O_3Br_4$(%); C, 18.33; H, 5.39; N, 14.25. Found: C, 19.07; H, 5.89; N, 14.53.

X-ray Crystallography

The intensity data were collected with an Enraf-Nonius CAD-4 diffractometer at room temperature. SHELXS-86 [40] and SHELXL-93 [41] were used to solve and refine the structures, respectively. All non-hydrogen atoms were refined anisotropically except for the oxygen of the water molecule in **II**, which suffers from severe disorder. The hydrogen atoms of the bridging hydroxyl group in **II** and of the water molecules in **I** were located from a difference electron density map and refined isotropically, with the bond distances restrained to 0.85(3) Å. In both structures, the remaining hydrogen atoms were placed in their geometrically ideal position with isotropic temperature factors 1.2 times those of their attached non-hydrogen atoms. Hydrogen atoms of the disordered water molecule in **II** could not be located from difference maps. Refinement of the absolute structure parameter [42] of **I**, resulted in the value of 0.2413(0.0282) suggesting inversion twins with approximately 24% of the inverted component. Therefore, refinement of racemic twinning was performed, and improvements in the R-factors and GOF were observed. A relatively deep hole found in the final difference map of **II** was ignored since it is too close to Br(1). Parameters for data collection and structure refinements are summarized in Table I and selected bond lengths and angles are listed in Table II.

RESULTS AND DISCUSSION

Complexes [*cis*-β-Cr(trien)(C_2O_4)]Cl $\cdot$ $2H_2O$ (**I**) and [$Cr_2(\mu\text{-}OH)_2(\mu\text{-}tren)_2$]$Br_4 \cdot 2H_2O$ (**II**) were prepared *via* [Cr(trien)Cl_2]Cl and [Cr(tren)Cl_2]Cl, respectively. The dichloro complexes were obtained in reasonable yield by the reaction of chlorodimethylsulfoxide-chromium(III) [39] with trien, or trien, in DMSO at 150°C, followed by the addition of conc. HCl. The oxalato complex **I** was recrystallized from an aqueous solution containing equimolar amounts of [Cr(trien)Cl_2]Cl and sodium oxalate. However, slow crystallization of an aqueous solution of [Cr(tren)Cl_2]Cl and two equivalents of $NaNO_2$ in presence of NaBr afforded the dinuclear complex **II**. In spite of the fact that we intended to synthesize [Cr(tren)$(NO_2)_2$]Br, and failed to produce it, another equally interesting compound was obtained. The slightly basic medium caused by $NaNO_2$ seemed to be enough to generate the very small amounts of the hydroxide ions needed for the base hydrolysis of the dichloro compound.

TABLE I Summary of data collection and refinements

	I	*II*
Formula	$C_8H_{22}ClCrN_4O_6$	$C_6H_{21}Br_2CrN_4O_2$
F.w.	357.75	393.09
Crystal system	Monoclinic	Monoclinic
Space group	*Pn*	$P2_1/n$
a (Å)	7.193(2)	10.835(2)
b (Å)	9.1545(12)	7.859(3)
c (Å)	11.469(2)	16.397(2)
β (°)	100.994(13)	105.45(2)
V (Å^3)	741.3(3)	1345.7(5)
Z	2	4
D_{calc} (g/cm^3)	1.603	1.940
μ (mm^{-1})	0.981	6.779
F(000)	374	780
Crystal size (mm^3)	$0.66 \times 0.22 \times 0.17$	$0.25 \times 0.33 \times 0.48$
2θ range (°)	4–60	4–50
Index ranges (h, k, l)	$\pm 10, +12, +16$	$\pm 12, +9, +19$
Reflections collected	2251	2467
Independent (R_{int})	2251 (0.0000)	2385 (0.0339)
Observed [$I > 2\sigma(I)$]	1441	1450
Transmission	0.9942–0.8676	0.9949–0.5589
Data/restraints/parameters	2251/6/197	2385/1/135
GOF on F^2[b]	0.916	1.059
Final R indices[c] [$I > 2\sigma(I)$]	$R_1 = 0.0338$, $wR_2 = 0.0764$	$R_1 = 0.0481$, $wR_2 = 0.1408$
R indices (all data)	$R_1 = 0.0744$, $wR_2 = 0.0850$	$R_1 = 0.0932$, $wR_2 = 0.1558$
Largest diff. peak/hole (e/Å^3)	0.380 and -0.333	0.838 and -1.519

[a] Common for both structures: room temperature, $\lambda = 0.71073$ Å (MoK_α), absorption correction by ψ-scans, refinements by full-matrix least squares on F^2.

[b] $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(\text{no. of reflections} - \text{no. of parameters refined})\}^{1/2}$

[c] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$; $w = 1/[\sigma^2 F_o^2 + (nP)^2]$ *where* $P = (F_o^2 + 2F_o^2)/3$

TABLE II Selected bond lengths (Å) and angles (°)

I		*II*	
Cr–O(2)	1.953(3)		
Cr–O(1)	1.955(3)	Cr(1)–O(1)#1	1.942(4)
Cr–N(3)	2.060(3)	Cr(1)–O(1)	1.943(4)
Cr–N(1)	2.079(4)	Cr(1)–N(2)	2.068(5)
Cr–N(2)	2.078(4)	Cr(1)–N(3)	2.077(5)
Cr–N(4)	2.086(3)	Cr(1)–N(4)	2.093(6)
O(1)–C(1)	1.283(5)	Cr(1)–N(1)	2.139(5)
O(2)–C(2)	1.287(5)		
O(3)–C(1)	1.215(5)	N(2)–Cr(1)–N(1)	167.7(2)
O(4)–C(2)	1.225(5)	O(1)–Cr(1)–N(4)	171.4(2)
		O(1)–Cr(1)–N(3)	169.1(2)
N(2)–Cr–N(4)	163.0(2)	O(1)–Cr(1)–O(1)	78.7(2)
O(1)–Cr–N(1)	170.57(14)	O(1)–Cr(1)–N(1)	96.3(2)
O(2)–Cr–N(3)	174.07(14)	O(1)–Cr(1)–N(2)	90.4(2)
O(2)–Cr–O(1)	82.67(13)	O(1)–Cr(1)–N(4)	93.4(2)
O(1)–Cr–N(3)	91.41(14)	N(3)–Cr(1)–N(4)	97.3(2)
O(2)–Cr–N(1)	90.17(14)	O(1)–Cr(1)–N(1)	95.9(2)
N(3)–Cr–N(1)	95.7(2)	O(1)–Cr(1)–N(2)	95.6(2)
O(2)–Cr–N(2)	98.46(14)	O(1)–Cr(1)–N(3)	90.5(2)
O(1)–Cr–N(2)	92.61(14)	N(2)–Cr(1)–N(3)	91.5(2)
N(3)–Cr–N(2)	81.8(2)	N(2)–Cr(1)–N(4)	87.9(2)
N(1)–Cr–N(2)	82.3(2)	N(3)–Cr(1)–N(1)	83.9(2)
O(2)–Cr–N(4)	98.3(2)	N(4)–Cr(1)–N(1)	81.3(2)
O(1)–Cr–N(4)	92.0(2)		
N(3)–Cr–N(4)	81.7(2)	$1-x, -y, -z$	
N(1)–Cr–N(4)	95.1(2)		

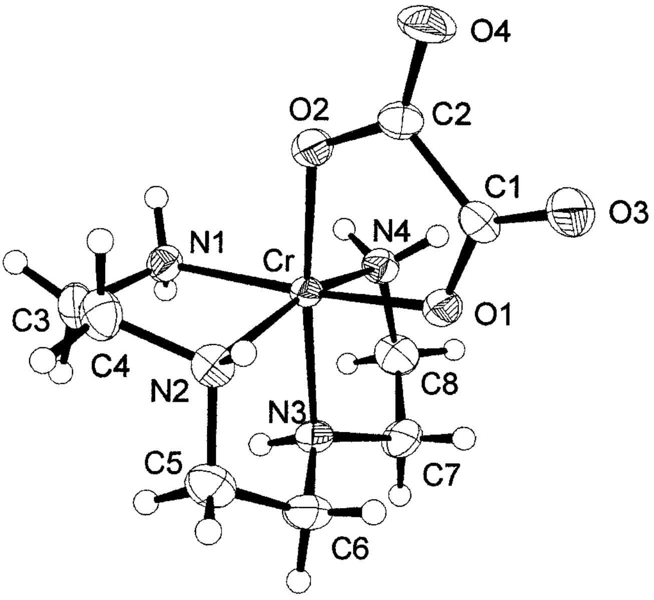

FIGURE 1 An ORTEP view of the cation of **I** shown at 50% probability level.

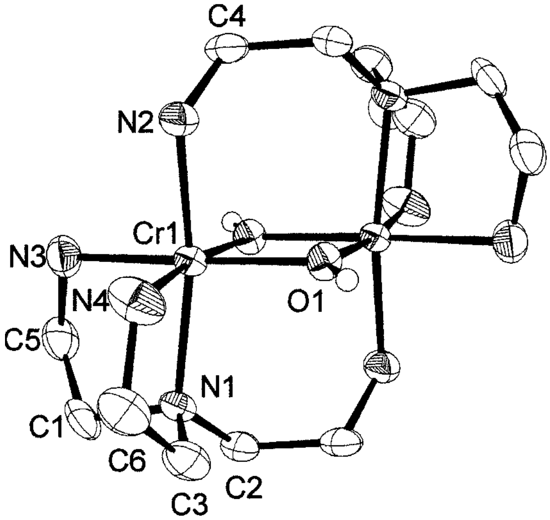

FIGURE 2 The structure of the cation of **II** shown at 50% probability level. Only crystallographically unique atoms have been labelled. Hydrogen atoms of the tren ligand have been omitted for clarity.

Figures 1 and 2 give labelled views for compounds **I** and **II**. The corresponding data collection and structural parameters for the two complexes are reported in Table I, whereas selected bond distances and angles are shown in Table II.

The oxalato complex **I** crystallizes as a racemate just as in the case of the cobalt (III) analogue [*cis*-β-Co(trien)(ox)]Cl · $3H_2O$ (**III**). [6] It has been found that the average Co–O(ox) and Co–N(amine) distances in **III** are 1.912 and 1.934 Å, respectively whereas in **I** the corresponding average values are 1.954 and 2.076 Å fo Cr–O (ox) and Cr–N(amine), respectively. Consequently, the larger bond distances obtained for the chromium complex **I** and its expected larger lability cannot be the explanation for the racemic crystallization of these compounds. In fact [*cis*-β-Cr(trien)(C_2O_4)] Br · $2H_2O$ has been observed by Kukina and Porai-Koshits to crystallize as a conglomerate [9]. This compound and our compound **I** have the same chromium cation, the same two water of crystallization and differ only in the counter anions. In order to find a clue that may explain the difference in the crystallization mode for the two compounds, we examined that coordinates of the bromide complex [9] from Cambridge Structural Database. We found that there is a very big difference in the hydrogen bonding patterns between the amine hydrogens, the most important difference being the hydrogen bonds between the amine hydrogens and waters of crystallization. Specifically the d(N$\cdots$O) in the chloride have distances of 2.848 and 2.863 Å, whereas in the case of bromide, they are much longer (2.967 and 3.028 Å).

In the past, we have noted that the ability of a transition metal complex (neutral cationic or anionic) to crystallize as a conglomerate is directly related to the ability of such species to form infinite helical strings [1–5,13,18,21,22]. Given the much stronger hydrogen bonds between the water of crystallization and the amine hydrogens in the case of chloride (**I**), one must expect much weaker hydrogen bonds between the non-bonded oxalato-oxygens and the amine-hydrogens of the adjacent metal cations, thus interfering with the formation of the helical strings observed in the past [1–5,13,18,21,22] as well as in the case of the bromide analogue [9]. We believe this discrepancy in the crystallization behavior between our chromium chloride and the corresponding bromide has its origin in the interference in the formation of helical strings normally present in conglomerates.

Finally, the average distances in the chromium complex **I** are distinctly longer than those in **III**. These results are somewhat puzzling since the $[NH_4][Cr(en)_2(ox)]Cl_2 \cdot H_2O$ [13] and $[OH_3][Co(en)_2(ox)]Cl_2 \cdot H_2O$ [21] crystallize as racemates, and the two compounds are isomorphous and isostructural and their fractional coordinates, and bond lengths and angles, are virtually identical [13,21]. We plan to investigate this discrepancy with additional pairs of chromium and cobalt compounds.

The structure of the binuclear complex **II** consists of $[Cr_2(\mu\text{-OH})_2(\mu\text{-tren})_2]^{4+}$ cations and four Br^- ions in the unit cell. The molecular structure and atom labelling scheme for the cation is illustrated in Fig. 2. The two Cr ions in the dimeric complex cation display distorted octahedral environments, formed by two bridged hydroxo ligands and four N-atoms. Three of the N-donors are supplied by one tren and the fourth coordination site is completed *via* a bridging aminoethyl arm of the neighboring tren binding the second chromium ion. Two primary amine nitrogen atoms form the basal plane of the octahedral structure, whereas the apical positions are occupied by the tertiary nitrogen atom N(1) of the tren and the primary nitrogen atom N(2) of the second bridged tren ligand. The Cr–O distance is 1.942(4) Å and the Cr–N distances are 2.068(5), 2.077(5), 2.093(6) and 2.139(5) Å. All the primary amine Cr–N distances are significantly shorter than the corresponding tertiary amine Cr–N(1).

Within the bridging moiety, the Cr···Cr separation is 3.005(2) Å, and the ∠Cr–O–Cr and ∠O–Cr–O bond angles are 101.3(2)° and 78.7(2)°, respectively, which clearly indicates pronounced ring strain in the four-membered ring of the molecule. Three N of each tren ligand are coordinated to one Cr ion and leaving one ethylamine arm free to span over and bind the second Cr(III) ion. It is interesting to note that a similar dinuclear species, $[Cr_2(\mu\text{-OH})(\mu\text{-CO}_3)(\mu\text{-tren})_2](ClO_4)_3 \cdot 2H_2O$ [16] was isolated from the reaction of $[Cr(tren)Cl_2]Cl$ and $AgNO_3$ at pH = 9. This hydroxo-carbonato complex was obtained by CO_2 fixation under atmospheric condition [16]. Binuclear and polynuclear metal complexes bridged by aliphatic chain amines are quire rare, but a few examples were found in the literature [15,37,38,43–46]. These include $[Ni_2(tren)_2\ (trien)](ClO_4)_4$ [37], $[Mn_2(\mu\text{-O})_2(\mu\text{-tren})_2](CF_3SO_3)_3$ [38], $[Cu(trpn)(N_3)]_n(ClO_4)_n$ [43], $[Cu_2(trpn)(tren)(NO_2)(H_2O)](ClO_4)_3$ [43], $[Cu(trpn)(NO_3)]_2(NO_3)_2$ [44], $[Cu(332)\ (NO_3)]_2(NO_3)_2$ [44] and $Na_2[(VO)_2(TTHA)] \cdot 10H_2O$ [45]. A common feature exists in most of these complexes, which is the fact that they were obtained with tripodal amine ligands.

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Supplementary Material

The CIF document filed with the Cambridge Structural Database as document No. CCDC 143281 and CCDC 133905 for **I** and **II**, respectively.

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