Table III. Extended Hückel Parameters[a]

		H_{ii}, eV	ζ_1^b	ζ_2^b	C_1^c	C_2^c
Mo	4d	-10.50	4.540	1.900	0.5899	0.5899
	5s	-8.34	1.960			
	5p	-5.24	1.900			
Cl	3s	-26.30	2.033			
	3p	-14.20	2.033			
C	2s	-21.40	1.625			
	2p	-11.40	1.625			
O	2s	-32.30	2.275			
	2p	-14.80	2.275			
H	1s	-13.60	1.300			

[a] Hückel constant k = 1.75. [b] Slater-type orbital exponents. [c] Coefficients used in double-ζ expansion.

Table IV. Bond Lengths (Å)

Mo–Mo	2.61	Mo–C	2.06
Mo–H	1.70	C–O	1.20
Mo–Cl	2.48		

widths for the earlier transition metals lead to additional inaccessible molecular orbitals derived from the d^6 band. The number of these inaccessible orbitals depends crucially on the relative disposition of the metal and bridging ligand polyhedra. When the ligands are located on the faces, the resultant spectrum of metal–metal bonding orbitals leads to a cluster valence electron counter of 84 (e.g. $[Mo_6Cl_{14}]^{2-}$). Related nido and arachno clusters have 68 and 52 valence electrons, respectively. When the ligands are located on the edges, the preferred electron count is 76 (e.g. $[Nb_6Cl_{18}]^{4-}$) and the related nido and arachno clusters have 66 and 56 valence electrons, respectively.

For both classes of clusters the removal of an M–Cl fragment leads to a decrease of five in the total number of metal–chlorine bonding molecular orbitals. In the face-bridged clusters the loss of the M–Cl fragment also destabilizes three of the bonding skeletal MO's, and consequently the total electron count drops by 16 for the loss of each metal atom. In contrast, the loss of an M–Cl fragment from the edge-bridged clusters does not affect the number of bonding skeletal MO's and the electron count is reduced by only 10. These differences have been interpreted in terms of both delocalized and localized bonding models.

Acknowledgment. The SERC is thanked for financial support.

Appendix

The extended Hückel method[21] was used in all calculations. Values of the parameters are given in Table III. Bond lengths are listed in Table IV.

Registry No. $[Mo_6Cl_{14}]^{2-}$, 51364-21-7; $[Mo_5Cl_{13}]^-$, 99727-63-6; $[Mo_4Cl_{12}]$ (square planar), 101349-43-3; $[Mo_6Cl_{18}]^{2+}$, 101375-16-0; $[Mo_5Cl_{17}]^{3-}$, 101349-44-4; $[Mo_4Cl_{16}]^{8-}$, 101349-45-5; $[Mo_4Cl_{12}]$ (butterfly), 101349-46-6.

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[21] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

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Chloro Complexes of Cobalt(III) and Chromium(III) with 2,2-Dimethyl-1,3-diaminopropane. Synthesis, Characterization, and Acid Hydrolysis Kinetics

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trans-$CoCl_2(Me_2tn)_2^+$ (ClO_4^- and $ZnCl_4^{2-}$ salts) and *mer*-$[CoCl(Me_2tn)(tri)]ZnCl_4$ (tri = $NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2$) have been isolated (after HCl workup) from the dioxygen oxidation of $CoCl_2\cdot 6H_2O$ and Me_2tn (1:2 mole ratio) in MeOH at room temperature. A similar reaction with an equivalent mixture of $CoCl_2\cdot 6H_2O$, Me_2tn, and en results in the isolation of *trans*-$[CoCl_2(Me_2tn)(en)]ClO_4$. The *trans*-$CoCl_2(Me_2tn)_2^+$ cation reacts with pyridine in aqueous solution to give *trans*-$CoCl(Me_2tn)_2(py)^{2+}$, which can be isolated as the $ZnCl_4^{2-}$ salt. Reaction of Me_2tn (2 mol) with $CrCl_3\cdot 6H_2O$ (1 mol) dehydrated in boiling DMF results in the precipitation of *trans*-$[CrCl_2(Me_2tn)_2]Cl$, and ClO_4^- and $ZnCl_4^{2-}$ salts can be obtained by metathesis. Kinetic parameters [$k_H(298)$ (s^{-1}), E_a (kJ mol^{-1}), ΔS^*_{298} (J K^{-1} mol^{-1})] for the loss of the first chloro ligand in 0.1 M HNO_3 from *trans*-$CoCl_2(Me_2tn)_2^+$, *trans*-$CoCl_2(Me_2tn)(en)^+$, *trans*-$CrCl_2(Me_2tn)_2^+$, and *mer*-$CoCl(Me_2tn)(tri)^{2+}$ are respectively 5.57×10^{-3}, 96.8 ± 2, +28 ± 4; 3.22×10^{-4}, 98.0 ± 1.2, +8.5 ± 3; 2.20×10^{-5}, 103.6 ± 1.3, +5 ± 2; and 1.30×10^{-3}, 75 ± 2, -57 ± 4.

Introduction

As part of a continuing program to investigate analogous Co(III) and Cr(III) complexes with polyamine ligands, we describe here some chloro complexes containing Me_2tn[1] bound to the central metals. This diamine, when acting as a bidentate ligand, will form a six-membered ring, and the properties of the resulting complexes can be compared with those of the unsubstituted tn systems.

The synthesis of Me_2tn,[2a] while not difficult, is time-consuming. *trans*-$CoCl_2(Me_2tn)_2^+$ was described in 1946;[2b] since that time, the ligand has become commercially available, and structural studies have now been reported for the Zn(II), Cd(II), and Hg(II) complexes.[3] The earlier work[4] on *trans*-$CoCl_2(Me_2tn)_2^+$ showed that the rate of loss of the first chloro ligand in acidic solution was considerably slower (10 times) than that from the corresponding complex containing the unsubstituted diamine (tn). This is the reverse of the situation for five-membered chelate ring complexes,[5] and the basis for this observation has never been adequately explained.[6]

We were also interested in reinvestigating the synthesis of *trans*-$CoCl_2(Me_2tn)_2^+$ as we have recently found[7-9] that chloro-

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[1] Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, ibn = $NH_2C(Me)_2CH_2NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, Me_2tn = 2,2-dimethyl-1,3-diaminopropane = dan = $NH_2CH_2C(CH_3)_2CH_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, py = pyridine, DMF = dimethylformamide.

[2] (a) Lambert, A.; Lowe, A. *J. Chem. Soc.* **1947**, 1517. (b) Bailar, J. C., Jr.; Work, J. B. *J. Am. Chem. Soc.* **1946**, *68*, 232.

[3] Cariati, F.; Ciani, G.; Menabue, L.; Pellacani, G. G.; Rassu, G.; Sironi, A. *Inorg. Chem.* **1983**, *22*, 1897.

[4] Pearson, R. G.; Boston, C. R.; Basolo, F. *J. Am. Chem. Soc.* **1953**, *75*, 3089.

[5] Alexander, M. D. *Inorg. Chem.* **1966**, *5*, 2084.

[6] Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1958; p 120.

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Table I. Visible Absorption Spectral Parameters

complex	solvent	λ, nm (ε, M^{-1} cm^{-1})						ref
		$CoCl(N_5)^{2+}$ Systems						
mer-$[CoCl(en)(tri\text{-}A)]ZnCl_4$[a]	0.1 M HNO_3	sh 510 (∼86)	max 475 (103)	min 402 (37.2)	max 355 (94.3)	min 328 (61.7)		*b*
mer-$[CoCl(en)(tri\text{-}B)]ZnCl_4$[c]	0.1 M HNO_3	max 536 (93)	sh 425 (∼40)	min 421 (25.8)	sh 352 (∼125)			*d*
mer-$[CoCl(ibn)(tri\text{-}C)]ZnCl_4$[e]	0.1 M HNO_3	max 489 (125)		min 414 (40.0)	max 363 (107)	min 342 (82.5)		*f*
mer-$[CoCl(tn)(tri\text{-}D)]ZnCl_4$[g]	0.1 M HNO_3	max 550 (54.5)	sh 500 (∼52)	min 422 (14.3)	max 370 (73.4)	min 340 (46.8)		*h*
mer-$[CoCl(Me_2tn)(tri\text{-}E)]ZnCl_4{\cdot}H_2O$[i]	0.1 M HNO_3	max 538 (67.2)	sh 490 (∼48)	min 425 (17.3)	max 370 (83.1)	min 345 (64.6)		*j*
trans-$[CoCl(Me_2tn)_2(py)]ZnCl_4{\cdot}H_2O$	0.1 M HCl	max 545 (37.8)	min 505 (32.2)	max 475 (34.1)	min 425 (19.6)	sh 365 (∼68)		*j*
trans-$CoCl(tn)_2(py)^{2+}$	0.1 M HNO_3	max 551 (40.2)	min 505 (33.1)	max 485 (34.3)	min 430 (17.5)	max 363 (67.4)	min 353 (66.5)	*k*
cis-$CoCl(tn)_2(A)^{2+}$	0.1 M $HClO_4$	max 540 (54)	min 430 (13)	max 372 (64)	min 338 (35)			*n*
		trans-$CoCl_2(N_4)^+$ Systems						
trans-$[CoCl_2(Me_2tn)_2]_2ZnCl_4$	DMF	max 640 (35)	min 550 (3)	sh 460 (∼30)	sh 385 (∼57)			*j*
trans-$[CoCl_2(Metn)_2]ClO_4{\cdot}H_2O$	3 M HCl	max 640 (33)	min 548 (11.5)	sh 450 (∼35.5)				*j*
trans-$[CoCl_2(Me_2tn)(en)]ClO_4$	1 M HCl	max 626 (38.6)	min 534 (3)	max 417 (42.0)	min 314 (39.1)			*j*
		trans-$CrCl_2(N_4)^+$ Systems						
trans-$[CrCl_2(Metn)_2]_2ZnCl_4$	0.1 M HNO_3	max 590 (20.3)	min 520 (2.7)	sh 450 (∼20.5)	max 390 (32.9)			*j*
trans-$CrCl_2(tn)_2{}^+$	0.1 M HNO_3	max 596 (25.5)	min 525 (8.9)	sh 457 (∼25)	max 398 (38.8)			*l*
trans-$CrCl_2(tn)(en)^+$	0.4 M HNO_3	max 588 (24.8)	min 523 (10.3)	sh 450 (∼29.6)	max 402 (41.3)			*m*

[a] tri-A = $NH_2CH_2CH_2N{=}CHCH_2NH_2$. [b] Reference 8. [c] tri-B = $NH_2CH_2CH_2N{=}CHC(CH_3)_2CH_2C(CH_3)_2NH_2$. [d] Harnett, M.; House, D. A., unpublished research. [e] tri-C = $NH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$. [f] Reference 7. [g] tri-D = $NH_2CH_2CH_2CH_2N{=}CHCH_2CH_2NH_2$. [h] Reference 9. [i] tri-E = $NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2$. [j] This research. [k] Reference 17. [l] Reference 22. [m] Couldwell, M. C.; House, D. A.; Powell, H. K. J. *Inorg. Chem.* **1973**, *12*, 627. [n] Reference 19. A = aliphatic monoamine, e.g. CH_3NH_2.

pentaaminecobalt(III) complexes of the form CoCl(diamine)(triamine)$^{2+}$ are important byproducts when 1:2 mole ratios of Co(II) and a diamine are oxidized. The triamine is a Schiff base ligand believed to be formed by oxidative deamination of 1 mol of diamine, followed by condensation of the resultant amino aldehyde, either in situ or by using the metal ion as a template, with a second mole of diamine.

Experimental Section

2,2-Dimethyl-1,3-propanediamine was purchased from Aldrich Chemical Co. and used as supplied. All other chemicals were the best reagent grade available. *Caution*! Although we have experienced no difficulties with the perchlorate salts of the complexes described here, these should be treated as potentially explosive and handled with care.

Visible absorption spectral parameters (Perkin-Elmer 550) are reported in Table I, and all data for ^{13}C NMR spectra are referenced to dioxane at 67.4 ppm.

***trans*-Bis[dichlorobis(2,2-dimethyl-1,3-propanediamine)cobalt(III)] Tetrachlorozincate(II) and *mer*-Chloro(2,2-dimethyl-1,3-propanediamine)(3,3,7,7-tetramethyl-1,5,9-triazanon-4-ene)cobalt(III) Tetrachlorozincate(II) Hydrate: *trans*-$[CoCl_2(Me_2tn)_2]_2ZnCl_4$ and *mer*-$[CoCl(Me_2tn)(NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2)]ZnCl_4{\cdot}H_2O$.** Dioxygen was bubbled through a methanol solution (200 mL) of $CoCl_2{\cdot}6H_2O$ (13.6 g) at room temperature, while the diamine (11.7 g) dissolved in methanol was added dropwise over 10 min. Some precipitation occurred, but after oxygenation for 1 h a purple-brown solution had formed. Dropwise addition of 12 M HCl (20 mL) resulted in the formation of green crystals (presumably *trans*-$[CoCl_2(Me_2tn)_2]Cl$), and, after ice-cooling, these (17.7 g, 83%) were collected by filtration, washed with 2-propanol, and air-dried. Samples of the perchlorate or tetrachlorozincate(II) salts were obtained by dissolving 2 g of the crude chloride in 30 mL of 0.1 M HCl at 30–40 °C, adding an equal volume of 12 M HCl, and then 5 mL of 70% $HClO_4$ or 5 g of solid $ZnCl_2$, respectively, followed by ice-cooling. Anal. Calcd for $[CoCl_2(C_{10}H_{28}N_4)]ClO_4{\cdot}H_2O$: C, 26.60; H, 6.69; N, 12.40. Found: C, 26.73; H, 6.84; N, 12.63. ^{13}C NMR spectrum (DMF): 49.58, 33.86, 24.38 ppm. Anal. Calcd for $[CoCl_2(C_{10}H_{28}N_4)]_2ZnCl_4$: C, 27.43; H, 6.45; N, 12.80. Found: C, 27.21; H, 6.25; N, 12.73.

$ZnCl_2$ (10 g) was added to the mother liquor, and after the mixture was allowed to stand for 3 weeks at room temperature in an open beaker, the red crystals that deposited (contaminated with some green *trans*-dichloro complex) were collected and washed with 2-propanol. Two recrystallizations from 0.1 M HCl, as the $ZnCl_4{}^{2-}$ salt by addition of $HCl/ZnCl_2$, gave the pure chloropentaamine hydrate (0.7 g). Anal. Calcd for $[CoCl(C_{15}H_{37}N_5)]ZnCl_4{\cdot}H_2O$: C, 29.68; H, 6.47; N, 11.54. Found: C, 29.53; H, 6.47; N, 11.32.

***trans*-Chlorobis(2,2-dimethyl-1,3-propanediamine)(pyridine)cobalt(III) Tetrachlorozincate(II) Hydrate: $[CoCl(Me_2tn)_2(py)]ZnCl_4{\cdot}H_2O$.** Pyridine (2 mL) was added to an aqueous solution (10 mL) of *trans*-$[CoCl_2(Me_2tn)_2]_2ZnCl_4{\cdot}H_2O$ (1 g). A white precipitate ($Zn(OH)_2$?) deposited, and the solution color slowly changed to pink. After 24 h at room temperature, HCl (5 mL, 12 M) was added and then $ZnCl_2$ (2 g) at 40 °C. On cooling, a mixture of red and green crystals deposited, and one recrystallization as the $ZnCl_4{}^{2-}$ salt gave 0.5 g of the pure chloropentaamine. Anal. Calcd for $[CoCl(C_{10}H_{28}N_4)(py)]ZnCl_4{\cdot}H_2O$: C, 29.87; H, 5.87; N, 11.61. Found: C, 29.79; H, 5.67; N, 11.56. ^{13}C NMR spectrum (0.1 M HNO_3): 154.1 (py), 142.9 (py), 129.8 (py), 50.01 (NH_2CH_2–), 25.79 (>*C*$(CH_3)_2$), 25.79 (–CH_3), 22.19 (–CH_3) ppm.

***trans*-Chlorobis(1,3-propanediamine)(pyridine)cobalt(III) Tetrachlorozincate(II)** was prepared similarly from *trans*-$[CoCl_2(tn)_2]_2ZnCl_4$. ^{13}C NMR spectrum (0.1 M HNO_3): 154.3 (py), 142.6 (py), 129.5 (py), 39.6 (NH_2CH_2–), 26.0 (–$CH_2CH_2CH_2$–) ppm.

***trans*-Dichloro(2,2-dimethyl-1,3-propanediamine)(1,2-diaminoethane)cobalt(III) Perchlorate.** Dioxygen was bubbled through a solution of $CoCl_2{\cdot}6H_2O$ (4.76 g) in water (50 mL) to which had been added a solution of Me_2tn (2.04 g) and en (1.36 g) in water (10 mL). After 2 h the brown oxidized solution was warmed on a steam bath and HCl (12 M, 10 mL) was added. The now green solution was heated to ca. 60 °C,

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(7) McKee, V.; Harnett, M.; House, D. A. *Inorg. Chim. Acta* **1985**, *102*, 83.

(8) House, D. A. *Helv. Chim. Acta* **1985**, *68*, 1872.

(9) Reisen, A.; Zehnder, M.; House, D. A. *Inorg. Chim. Acta*, in press.

Table II. Experimental Details for the Spectrophotometrically Determined Rate of Loss of the First Chloro Ligand from Co(III) and Cr(III) Complexes of Me_2tn in 0.1 M HNO_3

cation	anion	isosbestic points, nm	λ,[a] nm
trans-$CoCl_2(Me_2tn)_2^+$	$ZnCl_4^{2-}$	600, 480, 405, 360	640
trans-$CoCl_2(Me_2tn)(en)^+$	ClO_4^-	599, 471, 411, 353	570[b]
trans-$CrCl_2(Me_2tn)_2^+$	$ZnCl_4^{2-}$	585, 435, 408	550[b]
mer-$CoCl(Me_2tn)(tri)^{2+}$[c]	$ZnCl_4^{2-}$	520, 415, 368	560

[a] Wavelength used to monitor the reaction. [b] An isosbestic point for the second solvolysis step. [c] tri = $NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2$.

Table III. Observed and Calculated First-Order Rate Constants (s^{-1}) for the Loss of the First Chloro Ligand from *trans*-$MCl_2(AA)_2^+$ Cations in 0.1 M HNO_3

T, °C	10^4k_{obsd}[a]	10^4k_{calcd}[b]
	trans-$CoCl_2(Me_2tn)_2^+$[c]	
19.0 (1)[d]	25.1 ± 2	25.0
23.3 (2)	44.4 ± 2	44.6
25.0		55.7
25.2 (2)	56.6 ± 3	57.2
27.8 (2)	79 ± 4	80.2
30.2 (2)	113 ± 6	109
32.4 (1)	140 ± 7	144
	trans-$CoCl_2(en)(Me_2tn)^+$[e]	
25.0		3.22
31.2 (1)	7.03 ± 0.8	7.20
35.5 (3)	12.5 ± 0.3	12.4
41.0 (2)	24.0 ± 1	24.1
45.5 (1)	40.8 ± 2	40.9
	trans-$CrCl_2(Me_2tn)_2^+$[f]	
25.0		0.220
35.0 (1)	0.87 ± 0.04	0.853
50.1 (1)	5.47 ± 0.02	5.64
54.8 (1)	9.59 ± 0.01	9.81
58.8 (1)	15.5 ± 0.7	15.5
62.2 (1)	23.5 ± 1.3	22.7
	mer-$CoCl(Me_2tn)(tri)^{2+}$[g]	
25.0 (1)	13.1 ± 0.8	13.0
30.8 (1)	22.7 ± 1.2	23.1
31.2 (1)	23.9 ± 0.7	24.0
36.0 (1)	38.5 ± 1.7	38.0

[a] Mean ± standard deviation. [b] Calculated from the activation parameters cited in Table V. [c] Complex used was *trans*-$[CoCl_2(Me_2tn)_2]_2ZnCl_4$. [d] Number of determinations in parentheses. [e] Complex used was *trans*-$[CoCl_2(en)(Me_2tn)]ClO_4{\cdot}H_2O$. [f] Complex used was *trans*-$[CrCl_2(Me_2tn)_2]_2ZnCl_4$. [g] Complex used was *mer*-$[CoCl(Me_2tn)(tri)]ZnCl_4{\cdot}H_2O$; tri = $NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2$.

Table IV. Kinetic Parameters for the Loss of the First Chloro Ligand from *trans*-$MCl_2(N_4)^+$ Systems in Aqueous Acidic Solution (25.0 °C)

N_4	$[H^+]$, M	10^4k, s^{-1}	E_a, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ref
		M = Co(III)			
$(en)_2$	0.01	0.32	111.8	+44	*a*
(en)(ibn)	0.1	2.3	96.9	+2	*b*
(en)(Me_2tn)	0.1	3.22	98.0 ± 1.2	+8.5 ± 3	*c*
(en)(tn)	0.3	3.96	101.3	+21.3	*d*
t-$(ibn)_2$[e]	1.0	9.94	106	+45	*f*
c-$(ibn)_2$[e]	1.0	30.7	93.6	+13	*f*
$(Me_2tn)_2$	0.1	55.7	96.8 ± 2	+28 ± 4	*c*
$(tn)_2$	?	553	89	+29	*g*
		M = Cr(III)			
$(en)_2$	0.1	0.225	97.0	−17	*h*
(en)(tn)	0.4	0.193	97.8	−15	*d*
$(Me_2tn)_2$	0.1	0.220	103.6 ± 1.3	+5 ± 2	*c*
$(tn)_2$	0.1	0.208	102.4	+0.4	*i*
		mer-$CoCl(Me_2tn)(tri)^{2+}$[j]			
	0.1	13.0	75 ± 2	−57 ± 4	*c*

[a] Daffner, G.; Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1982**, *61*, 57 (μ = 0.1 M). [b] Harnett, M.; House, D. A., unpublished research. [c] This research. [d] Couldwell, M. C.; House, D. A.; Powell, H. K. J. *Inorg. Chem.* **1973**, *12*, 627. [e] *t* = *trans-gem*-dimethyl, *c* = *cis-gem*-dimethyl. [f] Harnett, M.; House, D. A.; Robinson, W. T. *Inorg. Chim. Acta* **1985**, *102*, 87. [g] Jonasson, I. R.; Murray, R. S.; Stranks, D. R.; Yandell, J. K. *Proc. Int. Conf. Coord. Chem.* **1969**, *12*, 32. [h] MacDonald, D. J.; Garner, C. S. *J. Inorg. Nucl. Chem.* **1961**, *18*, 219. [i] Reference 22. [j] tri = $NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2$.

and the addition of $HClO_4$ (60%, 10 mL) resulted in the precipitation of ca. 3 g of green crystals, which, after ice-cooling, were collected, washed with 2-propanol and then ether, and air-dried. The product was recrystallized from a minimum volume of 60 °C 0.1 M HCl on the addition of equal volumes of HCl (12 M) and $HClO_4$ (60%). Anal. Calcd for $[CoCl_2(C_7H_{22}N_4)]ClO_4$: C, 21.46; H, 5.60; N, 14.31. Found: C, 21.45; H, 5.20; N, 14.05. ^{13}C NMR spectrum (DMF): 49.37, 45.90, 30.82, 24.35 ppm.

***trans*-Dichlorobis(2,2-dimethyl-1,3-propanediamine)chromium(III) Salts: *trans*-$[CrCl_2(Me_2tn)_2]X$.** $CrCl_3{\cdot}6H_2O$ (5 g) was heated in DMF (40 mL) until the temperature of solution reached 145 °C (and the volume had been reduced to about 30 mL). The neat amine (4 mL) was added dropwise with stirring to give a dichroic violet/green solution, which was allowed to cool slowly. Green crystals (2.7 g) deposited at 120 °C, when the wall of the flask was scratched with a glass rod. After ice-cooling, the (presumably) *trans*-$[CrCl_2(Me_2tn)_2]Cl$ was collected, washed with 2-propanol and acetone, and air-dried. The crude chloride salt was recrystallized as the perchlorate or $ZnCl_4^{2-}$ salt, as for the Co(III) analogue. Anal. Calcd for $[CrCl_2(C_{10}H_{28}N_4)]_2ZnCl_4$: C, 27.88, H, 6.55; N, 13.01. Found: C, 28.71, H, 6.66; N, 13.33.

Kinetics. The rates of loss of the first chloro ligand in aqueous acidic solution (0.1 M HNO_3) for four of the complexes prepared here have been measured spectrophotometrically. Experimental details are given in Table II, and first-order rate constants [k_{obsd} (s^{-1})] (Table III) were calculated from absorbance vs. time plots at fixed wavelengths. Activation parameters (Table IV) were calculated[10] from the variation of k_{obsd} with temperature.

Results and Discussion

Co(III) Complexes. Dioxygen oxidation of $CoCl_2{\cdot}6H_2O$ and Me_2tn (1:2 mole ratio) in methanol, followed by HCl workup, results in the isolation of green *trans*-$CoCl_2(Me_2tn)_2^+$ and a red chloropentaamine, $CoCl(C_{15}N_{37}N_5)^{2+}$. This latter product, formed in small amounts, is the Me_2tn analogue of a series of recently isolated complexes of general formula *mer*-CoCl(diamine)(tridentate Schiff base)$^{2+}$,[7-9] where the diamine can be en, ibn, or tn (Table V). In this case, the red product is formulated as *mer*-$[CoCl(Me_2tn)(NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2)]ZnCl_4{\cdot}H_2O$ by analogy with the tn and ibn analogues, whose crystal structures have recently been determined.[7,9] The ^{13}C NMR spectrum of this material is complex, and all 15 C atoms can be accounted for, with the characteristic >C=N− carbon resonance at 189.02 ppm (cf. resonances at 181.84, 184.95, and 183.2 ppm for the related en, ibn, and tn complexes, respectively).

The chloro ligand in $CoCl(Me_2tn)(C_{10}H_{23}N_3)^{2+}$ is remarkably labile for a chloropentaamine, with a half-life of ca. 9 min at 25 °C in 0.1 M HNO_3 ($k_H = 1.30 \times 10^{-3}$ s^{-1}). This is about 12 times faster than that of the tn analogue $CoCl(tn)(C_6H_{15}N_3)^{2+}$ (Table V), which, in turn, is about 6 times faster than that of the fully saturated six-membered-ring analogue *mer*-$CoCl(tn)(dpt)^{2+}$.[11] Thus, in this particular instance, the methyl substituents on the six-membered ring produce the anticipated acceleratory effect.

This is not the case, as first observed by Pearson et al.,[4] for the *trans*-$CoCl_2(Me_2tn)_2^+$ cation, relative to *trans*-$CoCl_2(tn)_2^+$, with half-lives of 122 and 13 s for the loss of the first chloro ligand in dilute aqueous acid, respectively, at 25 °C. Although both complexes aquate with considerable stereochemical change, the relative cis:trans ratios of $CoCl(AA)_2(OH_2)^{2+}$ in the products (AA

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Table V. Observed or Estimated Rate Constants for the Thermal and Hg^{2+}-Assisted Chloride Release for *mer*-$CoCl(diamine)(triamine)^{2+}$ Systems at 25.0 °C

diamine	triamine	k_{Hg}, M^{-1} s^{-1}	k_H, s^{-1}	ref[a]
ibn	$NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$	1.33×10^{-3}	$\sim 3 \times 10^{-8}$	*b, c*
en	dien	5.21×10^{-3}	1.78×10^{-7}	*d, d*
en	$NH_2CH_2CH_2N{=}CHCH_2NH_2$	2.43×10^{-2}	$\sim 6 \times 10^{-7}$	*e, c*
tn	dien	2.50×10^{-1}	5.65×10^{-6}	*f, g*
en	$NH_2CH_2CH_2N{=}C(CH_3)CH_2C(CH_3)_2NH_2$	3.66×10^{-1}	$\sim 1 \times 10^{-5}$	*h, c*
tn	dpt	$\sim 6.1 \times 10^{-1}$	1.74×10^{-5}	*c, g*
tn	$NH_2CH_2CH_2CH_2N{=}CHCH_2CH_2NH_2$	~ 3.4	1.04×10^{-4}	*c, i*
Me_2tn	$NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2$	~ 39	1.30×10^{-3}	*c, j*

[a] First entry for k_{Hg}, second entry for k_H. [b] Reference 7. [c] Estimated from the relationship $\log k_{Hg} = 0.96 \log k_H + 4.36$: House, D. A. *Inorg. Chim. Acta* **1981**, *51*, 273. [d] Huan, T. K.; Mulvihill, J. N.; Gainsford, A. R.; House, D. A. *Inorg. Chem.* **1973**, *12*, 1517. [e] Reference 8. [f] House, D. A. *Inorg. Chim. Acta* **1981**, *51*, 273. [g] Reference 11. [h] Harnett, M.; House, D. A., unpublished research. [i] Reference 9. [j] This research.

= tn, Me_2tn) are unknown. In both cases, the six-membered rings can adopt the cis configuration, e.g. in $(AA)_2Co(OH,O_2)Co(AA)_2^{3+}$[12] or $Co(ox)(AA)_2^+$,[13,14] but the relative rate difference between *trans*-$CoCl_2(Me_2tn)_2^+$ and *trans*-$CoCl_2(tn)_2^+$ suggests that the former may be more difficult to distort to a trigonal-bipyramidal intermediate and hence less readily aquated via a dissociative mechanism.[14,15] Indirect support for this postulate comes from a comparison of the *trans*-$CoCl_2(en)(tn)^+$ and *trans*-$CoCl_2(en)(Me_2tn)^+$ systems. Here there is little difference in k_{obsd} at 25 °C (Table IV), suggesting that the degrees of distortion in the dissociative intermediates are comparable.

Pyridine reacts with both *trans*-$CoCl_2(tn)_2^+$[16,17] and *trans*-$CoCl_2(Me_2tn)_2^+$ in aqueous solution to give chloropentaamine complexes of the type $CoCl(AA)_2(py)^{2+}$. Generally, this reaction produces $CoCl(AA)_2(py)^{2+}$ complexes in the cis configuration,[18] but the visible absorption spectra of the above pyridine complexes (Table I) are considerably different from those reported for *cis*-$CoCl(tn)_2(A)^{2+}$ (A = aliphatic monoamine).[19] Indeed, the large splitting of the first absorption band (550–480 nm) is more reminiscent of *trans*-$CoCl(en)_2(NH_3)^+$.[20] The ^{13}C NMR spectra of $CoCl(AA)_2(py)^{2+}$ (AA = tn, Me_2tn) provides more convincing evidence of a trans configuration, as the relatively simple aliphatic carbon resonance pattern indicates that both six-membered rings in the complex are identical, in contrast to the more complicated aliphatic carbon resonance pattern observed for tn in *cis*-$CoCl(tn)_2(A)^{2+}$ (A = aliphatic monamine).[19]

Cr(III) Complexes. The now standard method of reacting Me_2tn (2 mol) with $CrCl_3{\cdot}6H_2O$ (1 mol) dehydrated in boiling DMF produced a reasonable yield of green *trans*-$[CrCl_2(Me_2tn)_2]Cl$, which could be recrystallized as the $ZnCl_4^{2-}$ salt. A similar reaction with tn produces the corresponding *trans*-$[CoCl_2(tn)_2]Cl$, which is more easily isolated from the reaction mixture than in an earlier synthetic procedure using Me_2SO.[21,22]

It has been shown previously that Cr(III) complexes of general formula *trans*-$CrCl_2(AA)_2^+$ (AA = aliphatic diamine) aquate with rates almost independent of the nonreplaced ligand, and *trans*-$CrCl_2(Me_2tn)_2^+$ is no exception (Table IV).

We have no evidence for Cr–N bond rupture or isomerization during the course of this reaction, and the activation parameters are similar to those reported for *trans*-$CrCl_2(tn)_2^+$.[22]

This general independence of the aquation rate of *trans*-$CrCl_2(AA)_2^+$ complexes with respect to the nonreplaced ligand is attributed to a more associative mechanism for Cr(III) complexes when compared to their Co(III) analogues, where the nonreplaced ligand has a major influence on the aquation rate.[23]

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Registry No. *trans*-$[CoCl_2(Me_2tn)_2]_2ZnCl_4$, 101225-17-6; *mer*-$[CoCl(Me_2tn)(tri\text{-}E)]ZnCl_4$, 101225-19-8; *trans*-$[CoCl_2(Me_2tn)_2]ClO_4$, 101225-20-1; *trans*-$[CoCl(Me_2tn)_2(py)]ZnCl_4$, 101225-22-3; *trans*-$[CoCl(tn)_2(py)]ZnCl_4$, 101225-24-5; *trans*-$[CoCl_2(tn)_2]_2ZnCl_4$, 101247-94-3; *trans*-$[CoCl_2(Me_2tn)(en)]ClO_4$, 101225-26-7; *trans*-$[CrCl_2(Me_2tn)_2]_2ZnCl_4$, 101225-28-9; *mer*-$[CoCl(en)(tri\text{-}B)]ZnCl_4$, 101225-30-3.

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