135. The Crystal and Molecular Structure of $[Co(tmen)_3](C_7H_7SO_3)_3 \cdot 2\ H_2O$ and $[Co(tmen)_3](CH_3SO_3)_2 \cdot EtOH \cdot \frac{1}{2}\ H_2O$ (tmen = 2,3-Dimethylbutane-2,3-diamine)

by **Hans Brunner** and **Andreas Ludi***

Institut für Anorganische Chemie, Universität Bern, CH–3000 Bern 9

and **Andrea Raselli** and **Hans-Beat Bürgi**

Laboratorium für chemische und mineralogische Kristallographie, Universität Bern, CH–3000 Bern 9

(28.VI.96)

The molecular structure of the two complex ions $[Co(tmen)_3]^{3+}$ and $[Co(tmen)_3]^{2+}$ (tmen = 2,3-dimethylbutane-2,3-diamine) have been determined at 100 K. They show a strong trigonal distortion of the octahedral CoN_6 core. The twist angle is 26.2(2.8)° for Co^{II} and 43.9(9)° for Co^{III}. Average Co–N distances are 2.193(13) Å (Co^{II}) and 1.997(2) Å (Co^{III}), 0.02 Å longer than for the main body of Co^{III} amines.

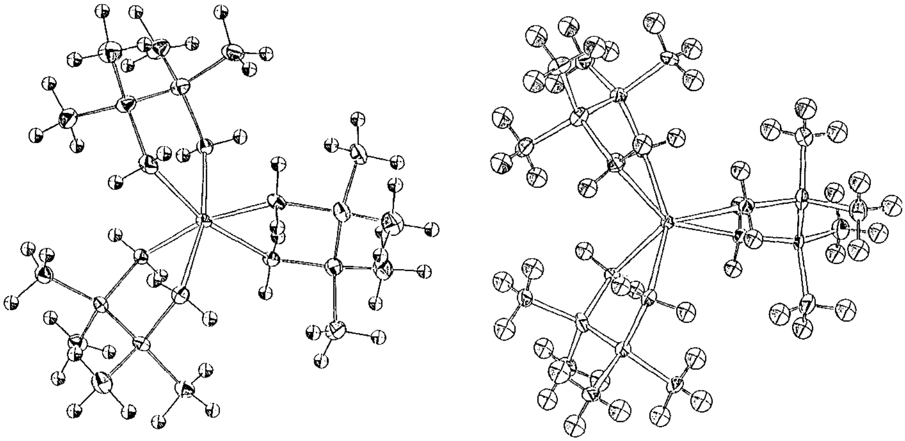
Introduction. – In contrast to the vast number of Co^{III} amines, $[Co(tmen)_3]^{3+}$ (tmen = 2,3-dimethylbutane-2,3-diamine, tetramethylethylenediamine) is a labile species with regard to base hydrolysis and racemization [1].

A smaller ligand-field strength [2] [3] and a higher reduction potential [2] imply a considerably expanded coordination cavity for tmen complexes compared to most other complex ions with a MN_6 core. Moreover, the spectroscopic results are compatible with a strong trigonal distortion of the coordination octahedron [3]. The synthesis of suitable crystalline samples of these coordination compounds and the subsequent crystal structure determination was undertaken to rationalize these observations.

Experimental. – *Synthesis and Crystal Growth.* $[Co(tmen)_3]^{3+}$ was prepared according to the procedure given in [4]. Crystals of $[Co(tmen)_3](tos)_3 \cdot 2\ H_2O$ (**1**; tos = *p*-toluenesulfonate, $C_7H_7SO_3^-$) were grown by slow evaporation of a sat. aq. soln. at r.t. Microcrystalline salts of $[Co(tmen)_3]^{2+}$ with a variety of counterions were obtained by reaction of the appropriate Co^{2+}_{aq} compound with an excess of tmen in EtOH. Crystals of $[Co(tmen)_3](CH_3SO_3)_2 \cdot EtOH \cdot \frac{1}{2}\ H_2O$ (**2**) were grown by cooling a sat. EtOH/MeOH (6:1) soln. from 50 to 4° under Ar. Densities were measured at 298 K by flotation.

The crystal of **1** was conventionally mounted on a quartz fiber, the crystal of **2** was sealed in a *Lindemann* capillary unter Ar. Both crystals (*Fig.*) were measured at *ca.* 100 K on an *Enraf-Nonius CAD-4* diffractometer equipped with a liquid N_2 attachment. Crystal data, conditions for data collection, and refinement parameters are given in *Tables 1* and *2*. Atomic scattering factors were taken from SDP [5], thermal motion corrections were calculated using THMA 11 [6]. Final atomic coordinates, bond lengths, and bond angles have been deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge, CB2 1EZ, England.

Structural Results. – The molecular structures of both coordination complexes consist of trigonally distorted $Co(tmen)_3$ chelates. The conformation of the chelate rings is ob_3 for both oxidation states. The trigonal distortion is measured by a twist angle which is 60° for octahedral and 0° for trigonal prismatic geometry. For **1**, the twist angle is 43.9(9)°, for **2** it is 26.2(2.8)°, *i.e.*, the Co^{II} complex is closer to the prismatic coordination than to the octahedral geometry. Expansion of the coordination cavity is demonstrated by long



$[Co(tmen)_3]^{3+}$ $[Co(tmen)_3]^{2+}$

Figure. *ORTEP Diagrams for the two complex ions* $[Co(tmen)_3]^{2+}$ *and* $[Co(tmen)_3]^{3+}$

Co–N distances within the CoN_6 core. The distance for compound **2** is 2.193(13) Å and that for **1** is 1.997(2) Å. Co^{II}–N distances for a variety of cobalt amines cluster around 2.17 Å, Co^{III}–N around 1.97 Å [7] [8]. The influence of steric crowding owing to the 12 peripheral Me groups is also reflected by the rather long C–C bond within the chelate ring, 1.551(5) Å (Co^{III}) and 1.559(13) Å (Co^{II}). Spectroscopic properties, redox behavior, and reactivity are thus fully compatible with the molecular structure of the two complexes.

A crucial parameter determining the energy barrier and hence the rate of $[Co(tmen)_3]^{3+/2+}$ electron transfer is Δr, the difference of the Co–N distances in the two oxidation states. For the two tmen complexes investigated in the present work, Δr is 0.20 Å, *i.e.*, virtually identical to the corresponding value of 0.19 Å for the $[Co(en)_3]^{3+/2+}$ pair [7]. In spite of this, the activation energy for electron self exchange is higher for $[Co(tmen)_3]^{3+/2+}$ than for $[Co(en)_3]^{3+/2+}$. We tentatively attribute this difference to an enhanced stiffness of the ligand environment imposed by the 12 Me groups.

We thank Dr. *Monnier*, *Ciba*, for a supply of tmen and the *Swiss National Science Foundation* for financial support (grant No. 20-29585-90).

Table 1. *Crystallographic Data for* **1**

Crystal data		*Data collection*	
$[Co(C_6H_{16}N_2)_3](C_7H_7SO_3)_3 \cdot 2\,H_2O$	MoK_α radiation	ω-Scan	$\theta_{max} = 25°$
$M = 957.1$	$\lambda = 0.71069$ Å	No absorption correction[a]	$h = 0 \rightarrow 11$
Triclinic	Cell parameters from 14 reflections	8145 measured independent reflections	$k = -19 \rightarrow +19$
$P\bar{1}$	$\theta = 10.8–14.5°$	6589 observed reflections, $[I > 3\sigma(I)]$	$l = -24 \rightarrow +24$
$a = 8.842(7)$ Å	$\mu = 5.8\ cm^{-1}$		3 check reflections every 100 reflections
$b = 14.850(12)$ Å	$T = 123$ K		intensity decay: none
$c = 19.137(7)$ Å	Parallelepiped	*Refinement*	
$\alpha = 106.4(5)°$	0.18 × 0.2 × 0.24 mm	Refinement on F	$w = 1/[\sigma^2(F_o) + 0.00109(F_o)^2]$
$\beta = 93.9(5)°$	pink	$R = 0.046$	$(\Delta/\sigma)_{max} = 0.04$
$\gamma = 103.0(6)°$		$wR = 0.051$	$\Delta\rho_{max} = 0.8e$ Å^{-3}
$V = 2326$ Å^3		Block diagonal refinement	$\Delta\rho_{min} = -0.3e$ Å^{-3}
$Z = 2$		6589 Reflections	
$D_x(123\ K) = 1.37\ gcm^{-3}$		729 Parameters	
$D_m = 1.35\ gcm^{-3}$		H-Atoms with fixed B's	

[a] Crystal shattered before performing the Ψ scans.

Table 2. *Crystallographic Data for* **2**

Crystal data		*Data collection*	
$[Co(C_6H_{16}N_2)_3](CH_3SO_3)_2 \cdot C_2H_5OH \cdot \frac{1}{2}\,H_2O$	MoK_α radiation	ω-Scan	$\theta_{max} = 25°$
$M = 653.8$	$\lambda = 0.71069$ Å	Absorption correction empirical	$h = 0 \rightarrow 19$
Orthorhombic	Cell parameters from 22 reflections	$T_{min} = 0.95$, $T_{max} = 0.97$	$k = 0 \rightarrow 21$
		3297 measured independent reflections	$l = 0 \rightarrow 13$
$P2_12_12$	$\theta = 14.3–18.3°$	2218 observed reflections, $[I > 3\sigma(I)]$	3 check reflections every 100 reflections
$a = 16.352(9)$ Å	$\mu = 7.0\ cm^{-1}$		intensity decay: none
$b = 18.275(9)$ Å	$T = 103$ K		
$c = 11.223(2)$ Å	Parallelepiped	*Refinement*	
$V = 3354$ Å^3	0.15 × 0.15 × 0.2 mm	Refinement on F	$w = 1.2833/[\sigma^2(F_o) + 0.000995(F_o)^2]$
$Z = 4$	violet	$R = 0.044$	$(\Delta/\sigma)_{max} = 0.03$
$D_x(103\ K) = 1.29\ gcm^{-3}$		$wR = 0.037$	$\Delta\rho_{max} = 0.5e$ Å^{-3}
$D_m = 1.24\ gcm^{-3}$		$S = 1.25$	$\Delta\rho_{min} = -0.4e$ Å^{-3}
		2218 Reflections	
		370 Parameters	
		H-Atoms with fixed B's	

REFERENCES

[1] H. Diab, P. Hendry, A. Ludi, K. B. Reddy, R. van Eldik, *Inorg. Chim. Acta* **1990,** *175,* 83.

[2] P. Hendry, A. Ludi, *J. Chem. Soc., Chem. Commun.* **1987,** 891.

[3] S. Brönnimann, A. Zilian, H. U. Güdel, A. Ludi, *Inorg. Chim. Acta* **1990,** *173,* 159.

[4] P. Hendry, A. Ludi, *Helv. Chim. Acta* **1988,** *71,* 1966.

[5] SDP, Structure Determination Package; Enraf-Nonius, Delft, The Netherlands, 1982.

[6] E. F. Maverick, K. N. Trueblood, Program THMA 11, Univ. of California, Los Angeles, USA, 1987.

[7] P. Hendry, A. Ludi, *Adv. Inorg. Chem.* **1990,** *35,* 117.

[8] J. M. Newman, M. Binns, T. W. Hambley, H. C. Freeman, *Inorg. Chem.* **1991,** *30,* 3499; R. M. L. Warren, K. J. Haller, A. Tatehata, A. G. Lappin, *ibid.* **1994,** *33,* 227.