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Acta Cryst. (1991). **C47**, 2310–2312

Structure of (1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)silver(II) Diperchlorate

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(Received 22 January 1991; accepted 7 May 1991)

Abstract. [Ag(C₁₄H₃₂N₄)](ClO₄)₂, *M_r* = 563·21, monoclinic, *P*₂₁/*n*, *a* = 9·2653 (7), *b* = 9·3626 (8), *c* = 12·8516 (8) Å, β = 90·740 (5)°, *V* = 1114·74 (13) Å³, *Z* = 2, *D_x* = 1·678 Mg m⁻³, λ(Mo *K*α) = 0·71073 Å, μ = 1·181 mm⁻¹, *F*(000) = 578, *T* = 296 K, *R* = 0·034 for 2789 independent reflections with *I* > 3σ(*I*). The structure is comprised of monomeric, centrosymmetric molecules, in which the silver atom is bound to the four nitrogen atoms of the macrocycle and also participates in weak axial interactions with two perchlorate oxygen atoms. The mean Ag—N bond length is 2·195 (3) Å and the Ag—O distance is 2·889 (4) Å.

Introduction. Two structure types are known for tetraaza macrocyclic complexes of silver(II). In [Ag(*tet a*)](NO₃)₂* (Mertes, 1978) and one isomer of [Ag(*cyclam*)](ClO₄)₂ (Ito, Ito & Toriumi, 1981), the silver is situated at a center of inversion and is bound

* Ligand abbreviations: *tet a* = *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; *cyclam* = 1,4,8,11-tetraazacyclotetradecane; *tmc* = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane.

to nitrogen atoms of the macrocycle in a square-planar configuration. Additional long interactions to an oxygen atom of each anion are present. In a second isomer of [Ag(*cyclam*)](ClO₄)₂, however, the silver is located on a mirror plane that bisects the two six-membered chelate rings and is displaced by 0·24 Å below the plane of the four nitrogen atoms (Ito, Ito & Toriumi, 1981). In this isomer, no axial interaction with the perchlorate is observed. Based on the EPR spectrum of [Ag(*tmc*)](ClO₄)₂(*g*_{||} < *g*_⊥), a possible structure with a folded ligand and a single coordinated perchlorate was suggested (Barefield & Mocella, 1973). In this paper, we report the crystal structure of [Ag(*tmc*)](ClO₄)₂.

Experimental. [Ag(*tmc*)](ClO₄)₂ was prepared according to the literature procedure (Barefield & Mocella, 1973; Trismiro & Po, 1988) by adding 5 mmol of the macrocycle to 10 mmol of silver perchlorate in 30 ml water and stirring for 1 h. The solution was then filtered and the filtrate was cooled at 278 K overnight. The needle-shaped dark orange-brown crystals were collected by vacuum filtration and washed with

cold distilled water followed by 5 ml of tetrahydrofuran. Data were collected on a Nicolet/Siemens *R3m/V* diffractometer from a fragment of dimensions $0.50 \times 0.33 \times 0.25$ mm that had been cut from a larger crystal. Unit-cell parameters were obtained from the setting angles of 50 reflections with $30 \leq 2\theta \leq 35^\circ$. Data collected for $4 \leq 2\theta \leq 60^\circ$ with $0 \leq h \leq 13$, $0 \leq k \leq 13$, $-18 \leq l \leq 18$, using the $\theta/2\theta$ scan technique. Absorption correction based on azimuthal scans; relative range of transmission factors 0.884–1.000. Three standard reflections (115, 332, 232) measured after each 97 data; linear decay of 3.5%. Total of 3347 reflections measured; 2679 with $I > 3.0\sigma(I)$. Structure solved by Patterson and difference Fourier methods. Computations employed a local modification of the UCLA Crystallographic Computing Package (Strouse, 1981) and portions of *SHELXTL-Plus88* (Sheldrick, 1988). Refinement based on F converged to $R = 0.034$, $wR = 0.065$, $S = 2.09$. Standard deviations estimated as described by Doedens & Ibers (1967) with $p = 0.05$; $w = 4F_o^2/\sigma^2(F_o^2)$. Maximum shift in final cycle = 0.19σ ; maximum peak on final difference Fourier map = $1.4 e \text{ \AA}^{-3}$ near silver. Scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were held in fixed, idealized positions with $C-H = 0.95 \text{ \AA}$. The total number of parameters refined was 133.

Discussion. Atomic parameters are listed in Table 1, while Table 2 contains bond distances and angles.* A view of the molecular structure is shown in Fig. 1. The complex is monomeric and centrosymmetric. The silver ion is bound to the four nitrogen atoms of the macrocycle and two perchlorate ions in a tetragonally elongated octahedral configuration. The Ag—O distance of 2.889 (4) Å is slightly longer than the corresponding distances in $[\text{Ag}(\text{cyclam})](\text{ClO}_4)_2$ [2.788 (2) Å] and $[\text{Ag}(\text{tet } a)](\text{NO}_3)_2$ [2.807 (4) Å]. The saturated tmc ligand system consists of two six-membered chelate rings in the chair conformation and two five-membered chelate rings in a slightly flattened *gauche* conformation. The four methyl groups consist of two pairs, one on each side of the AgN_4 coordination plane. This is the geometry that has been labelled *trans*-III for the analogous cyclam heterocycle (Bosnich, Tobe & Webb, 1965; Thom, Fox, Boeyens & Hancock, 1984). An analogous *trans*-III conformation has been reported for $\text{Zn}(\text{cyclam})(\text{ClO}_4)_2$ (Tyson, Hodgson, Hedman & Clark,

* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54236 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

U_{eq} = the mean of the eigenvalues of the U tensor.

	x	y	z	U_{eq}
Ag	0.0000	0.0000	0.0000	284 (2)
N(1)	0.0923 (3)	0.0701 (3)	-0.1478 (2)	351 (15)
N(2)	0.1014 (3)	0.1720 (3)	0.0912 (2)	367 (14)
C(1)	0.0654 (4)	0.2259 (4)	-0.1593 (3)	432 (19)
C(2)	0.1364 (5)	0.3181 (4)	-0.0741 (3)	480 (21)
C(3)	0.0740 (5)	0.3099 (4)	0.0341 (3)	439 (19)
C(4)	0.0140 (5)	0.1666 (4)	0.1887 (3)	475 (21)
C(5)	-0.0039 (6)	0.0143 (4)	0.2249 (3)	449 (21)
C(6)	0.2473 (5)	0.0361 (5)	-0.1636 (4)	490 (22)
C(7)	0.2583 (5)	0.1545 (5)	0.1160 (4)	565 (25)
Cl	0.3385 (1)	-0.2920 (1)	0.0265 (1)	445 (5)
O(1)	0.2555 (5)	-0.1657 (4)	0.0474 (3)	804 (26)
O(2)	0.4836 (4)	-0.2669 (6)	0.0539 (4)	997 (32)
O(3)	0.2815 (4)	-0.4024 (4)	0.0877 (3)	735 (23)
O(4)	0.3182 (5)	-0.3253 (5)	-0.0801 (3)	872 (27)

Table 2. Interatomic distances (Å) and angles ($^\circ$)

Ag—N(1)	2.194 (3)	Ag—N(2)	2.196 (3)
N(1)—C(1)	1.487 (5)	N(2)—C(3)	1.505 (5)
N(1)—C(5)	1.502 (5)	N(2)—C(4)	1.502 (5)
N(1)—C(6)	1.487 (5)	N(2)—C(7)	1.493 (5)
C(1)—C(2)	1.536 (6)	C(2)—C(3)	1.515 (6)
C(4)—C(5)	1.510 (5)	Ag—O(1)	2.889 (4)
Cl—O(1)	1.438 (4)	Cl—O(3)	1.406 (3)
Cl—O(2)	1.405 (4)	Cl—O(4)	1.415 (4)
N(1)—Ag—O(1)	90.9 (1)	N(2)—Ag—O(1)	86.4 (1)
N(1)—Ag—N(2)	94.2 (1)	Ag—N(2)—C(3)	107.5 (2)
Ag—N(1)—C(1)	108.2 (2)	Ag—N(2)—C(4)	100.9 (2)
Ag—N(1)—C(5)	101.4 (2)	Ag—N(2)—C(7)	116.2 (2)
Ag—N(1)—C(6)	116.2 (2)	C(3)—N(2)—C(4)	110.3 (3)
C(1)—N(1)—C(5)	111.2 (3)	C(3)—N(2)—C(7)	110.8 (3)
C(1)—N(1)—C(6)	110.9 (3)	C(4)—N(2)—C(7)	110.6 (3)
C(5)—N(1)—C(6)	108.5 (3)	N(2)—C(3)—C(2)	115.3 (3)
N(1)—C(1)—C(2)	114.3 (3)	N(2)—C(4)—C(5)	110.6 (3)
N(1)—C(5)—C(4)	110.8 (3)	O(1)—Cl—O(4)	107.3 (3)
C(1)—C(2)—C(3)	117.4 (3)	O(2)—Cl—O(3)	110.4 (2)
O(1)—Cl—O(2)	109.2 (3)	O(2)—Cl—O(4)	113.2 (3)
O(1)—Cl—O(3)	107.1 (2)	O(3)—Cl—O(4)	109.5 (3)

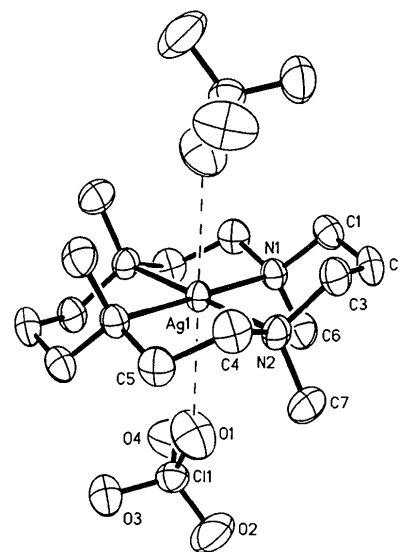


Fig. 1. View of the structure of $[\text{Ag}(\text{tmc})](\text{ClO}_4)_2$. Thermal ellipsoids are drawn at the 50% level.

1990); however, the Zn—O (perchlorate) distance of 2.380 (2) Å is considerably shorter than we observe.

The mean Ag—N bond distance of 2.195 (3) Å in [Ag(tmc)]²⁺ is slightly longer than the corresponding distances in Ag(tet a)²⁺ [2.160 (3) Å] and Ag-(cyclam)²⁺ [2.158 (2) Å]. This is presumably a result of cavity enlargement in tmc arising from ring strain caused by the methyl substituents.

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Acta Cryst. (1991). **C47**, 2312–2315

Structure of (4-Amino-2,2,6,6-tetramethylpiperidinyl-1-oxy)-bis(hexafluoroacetylacetonato)(methanol)nickel(II) Methanol Solvate

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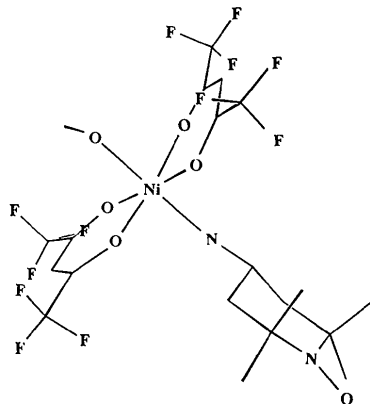
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(Received 6 September 1990; accepted 4 March 1991)

Abstract. [Ni(C₅H₂F₆O₂)₂(C₉H₁₇N₂O)(CH₃OH)]·CH₃OH, *M_r* = 707.2, monoclinic, *P*2₁/*n*, *a* = 12.125 (3), *b* = 12.379 (3), *c* = 20.438 (5) Å, β = 92.07 (2)°, *V* = 3066 (1) Å³, *D_x* = 1.532 Mg m⁻³, *Z* = 4, μ = 0.743 mm⁻¹, λ(Mo *K*α) = 0.71073 Å, *F*(000) = 1440, *T* = 298 K, *R* = 0.0678 and *wR* = 0.0912 for 2365 averaged reflections with *I* > 3σ(*I*). The Ni atom in this structure possesses an octahedral geometry and forms bonds to two equatorial F₆AcAc ligands, one molecule of methanol and the nitroxyl radical. Coordination of the nitroxyl is through the N atom of the amine group at a distance of 2.075 (6) Å. There are no unusual intermolecular contacts and the asymmetric unit contains a molecule of methanol.

Introduction. Nitroxyl radicals have been used extensively as spin labels in biological systems and, more recently, as ligands in the preparation of coordination compounds. The coordination behavior of these compounds is varied and diverse, examples of which include direct coordination through the O atom of the N—O group (Dickman & Doedens, 1981; Porter, Dickman & Doedens, 1983, 1985, 1988), and an η² type of coordination involving both the N and O atoms in reduced nitroxyls (Dickman & Doedens, 1982; Porter & Doedens, 1985). In instances where

substituted nitroxyl radicals such as 3-cyano-2,2,5,5-pyrrolidino-1-oxyl (TMPCN) have been used, coordination *via* the CN group has also been observed (Dickman & Doedens, 1983) including formation of a cocrystallized solid with no specific interactions involving the nitroxyl group (Porter & Doedens, 1984). In this paper we report the X-ray crystal structure of an Ni^{II} complex obtained from the reaction of Ni(F₆AcAc)₂ with 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, or simply 4-amino-TEMPO.



Experimental. The title compound was prepared by refluxing one equivalent of 4-amino-TEMPO with

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