pentacoordination of the Cu atom in molecule (1). The second water molecule, centered on O(10), is not associated with Cu(2). There are indications that the two water molecules form hydrogen bonds between the two molecules of the asymmetric unit, at 2·709 Å, and one forms a bond between ligands of molecules of adjacent asymmetric units, at 2·778 and 2·870 Å, with O—H···O angles of 167 to 176° (see Fig. 1).

The displacement of the structure of molecule (1) from the rectangular pyramid (r.p.) towards the trigonal bipyramid (t.b.p.) is simlar to that observed in copper quinaldinate monohydrate (Haendler, 1986). The transition characteristics and parameters for these systems, based on the Berry intramolecular ligand-exchange process, have been discussed by Holmes (1984) and Holmes & Deiters (1977). Unequal bond character (N *vs* O) favors axial-equatorial sites of t.b.p., and bidentate ligands permit some freedom of motion, in contrast to more rigid polydentate ligands. A comparison of the nine dihedral angles with idealized values places the complex on the Berry coordinate line, at 44% displacement from r.p. Table 3 lists the characterization parameters for the four atomic motions.

The author wishes to acknowledge receipt of a grant from the University of New Hampshire Research Office that made possible the use of the University Computation Center. The intensity data were collected by Dr Cynthia Day of Crystalytics Company, Lincoln, Nebraska.

Table 3. *Characteristic Berry ligand displacement motions* (°)

	Observed	Expected
N(1)—Cu(1)—N(3)	175·7	< 180
O(3)—Cu(1)—O(1)	154·8	> 120
O(3)—Cu(1)—O(9)	103·4	< 120
O(9)—Cu(1)—O(1)	101·9	< 120
δ_{24}*	20·3	$0 < \delta < 53·0$

* δ_{24} is the dihedral angle between the two faces of the t.b.p. that convert to the basal plane of the r.p.

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Acta Cryst. (1989). C**45**, 1694–1697

Structure of Azido(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(II) Perchlorate

By Steven Reimer and Mark Wicholas*

Department of Chemistry, Western Washington University, Bellingham, WA 98225, *USA*

and Brian Scott and Roger D. Willett*

Department of Chemistry, Washington State University, Pullman, WA 99164-4630, *USA*

(*Received* 27 *August* 1988; *accepted* 7 *March* 1989)

Abstract. $[Co(N_3)(C_{14}H_{32}N_4)]ClO_4$, $M_r = 456·83$, orthorhombic, $Pna2_1$, $a = 14·223$ (6), $b = 15·252$ (4), $c = 9·514$ (3) Å, $V = 2064$ Å^3, $Z = 4$, $D_x = 1·47$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·71069$ Å, $\mu = 9·92$ cm^{-1}, $F(000) = 964$, $T = 295$ K, $R = 0·049$, $wR = 0·047$, 2541 unique reflections. The structure consists of discrete $[Co(tetramethylcyclam)(N_3)]^+$ cations and ClO_4^- anions, the former containing five-coordinate cobalt(II) intermediate in geometry between trigonal bipyramidal and square pyramidal with the azide ion in the apical position of the distorted square pyramid.

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* To whom correspondence should be addressed.

0108-2701/89/111694-04$03.00

Introduction. The coordination chemistry of the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam) and its methylated homologue tetramethylcyclam (TMC) has been investigated frequently because of the stereochemical richness and potential for interconversion among each ligand's five possible configurational isomers (Barefield, Bianchi, Billo, Connolly, Paoletti, Summers & Van Derveer, 1986). For tetramethylcyclam, the ligand discussed herein, the most commonly studied stereoisomer of the five is '*trans*-I', using the Bosnich notation (Bosnich, Poon & Tobe, 1965), in which the four methyl groups are on the same side of the metal coordination plane as shown below. Although this stereoisomer is not the most thermodynamically stable, it appears to possess reasonable kinetic stability (Wagner & Barefield, 1976), and hence the *trans*-I configuration is retained under most conditions of metal-ion insertion. Our interest concerns the stereochemistry of five-coordinate-metal-ion complexes of *trans*-I TMC and the factors which determine whether the resulting geometry is square pyramidal (SPY), trigonal bipyramidal (TBP), or some intermediate thereof. To this end, we report the crystal structure of $[Co(TMC)(N_3)]ClO_4$ and compare it to that of the previously reported $[Ni(TMC)(N_3)]ClO_4$ (D'Aniello, Mocella, Wagner, Barefield & Paul, 1975).

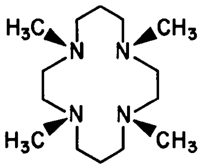

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Co	2622 (1)	6247 (1)	10971 (2)	32 (1)
Cl	3888 (1)	3019 (1)	10929 (3)	56 (1)
N(2)	2278 (3)	8133 (3)	10789 (7)	53 (2)
N(3)	2135 (3)	5445 (3)	9323 (5)	46 (1)
N(4)	3807 (3)	6519 (3)	9526 (5)	49 (1)
N(5)	3512 (3)	6202 (3)	12770 (5)	41 (1)
N(6)	2011 (3)	7408 (3)	10908 (8)	55 (1)
N(7)	2505 (4)	8858 (3)	10718 (11)	91 (4)
N(8)	1566 (3)	5691 (3)	12484 (5)	45 (1)
C(1)	4465 (4)	5832 (4)	12574 (7)	56 (2)
C(2)	5033 (4)	6222 (4)	11404 (8)	66 (3)
C(3)	4669 (4)	6021 (4)	9941 (7)	55 (2)
C(4)	3465 (5)	6187 (4)	8154 (7)	62 (2)
C(5)	2962 (6)	5340 (5)	8330 (7)	61 (2)
C(6)	1797 (4)	4542 (3)	9699 (8)	58 (2)
C(7)	1075 (4)	4478 (3)	10779 (9)	60 (2)
C(8)	1397 (4)	4740 (3)	12268 (7)	57 (2)
C(9)	2005 (4)	5841 (4)	13881 (7)	60 (2)
C(10)	3029 (5)	5662 (4)	13841 (7)	57 (2)
C(11)	3604 (4)	7115 (4)	13322 (7)	58 (2)
C(12)	4051 (5)	7461 (4)	9336 (9)	66 (2)
C(13)	1373 (5)	5907 (4)	8588 (8)	71 (3)
C(14)	649 (4)	6166 (4)	12488 (9)	69 (2)
O(1)	4221 (7)	3815 (4)	11270 (11)	185 (5)
O(2)	3713 (4)	3097 (4)	9436 (6)	100 (2)
O(3)	3029 (5)	2790 (5)	11457 (12)	191 (5)
O(4)	4545 (4)	2347 (3)	11189 (8)	100 (2)

Experimental. A solution of $Co(TMC)(ClO_4)_2$ was prepared by dissolving $Co(ClO_4)_2.6H_2O$ (142 mg, 0·390 mmol) and TMC (100 mg, 0·390 mmol) in 50% aqueous ethanol and, after heating, filtering to remove undissolved residue. A stoichiometric amount of solid sodium azide was added to yield a blue microcrystalline product which was recrystallized from methanol at 273 K. A crystal with dimensions 0·2–0·4 mm was selected for ω-scan data collection on a Nicolet *R3m/E* diffractometer system using Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1981). Cell dimensions were determined by least-squares refinement of 25 reflections in the range $25 < 2\theta < 30°$. Space group $Pna2_1$ (extinctions: $h0l$, h odd; $0kl$, $k+l$ odd). The noncentrosymmetric space group was chosen on the basis of the E-value statistics ($0·7 <$ average $|E^2 - 1| < 0·9$) and confirmed by the successful refinement. Three standards (111, 114, 121) were monitored every 100 reflections and showed no systematic variation: $R_{int} = 0·050$. No absorption corrections were made. Intensities of 2737 reflections were recorded ($2\theta \leq 40°$; $h \leq 10$, $k \leq 14$, $l \leq 15$) with variable (6–60° min^{-1}) scan speeds. After data reduction, there remained 2541 unique reflections and 2131 of these had $F > 3\sigma(F)$. The structure was solved *via* direct methods to yield the Co^{II} position, followed by subsequent cycles of structure-factor calculation and difference synthesis to locate the other atoms. Non-H atoms were refined anisotropically to $R = 0·049$ and $wR = 0·047$ based on 257 least-squares parameters, with a maximum $|\Delta|/\sigma = 0·040$, and $w^{-1} = \sigma^2(F_o) + 0·00059|F_o|^2$, $\sum w(|F_o| - |F_c|)^2$ minimized. The goodness of fit was 1·258. The H atoms were included with C—H distances fixed at 0·96 Å and isotropic thermal parameters approximately 20% larger than those of the C atoms to which they were bonded. The largest residual on the final difference map was 0·42 e $Å^{-3}$. All data reduction, structure solution and refinement, and graphics were executed using *SHELXTL* (Sheldrick, 1984) on an Eclipse S140 computer. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974). The final equivalent isotropic thermal and positional parameters are listed in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52018 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The title compound contains discrete $[Co(TMC)(N_3)]^+$ cations and perchlorate anions with four formula units per unit cell as shown in Fig. 1. Bond lengths and angles are presented in Table 2. The tetraaza ligand, TMC, adopts the expected *trans*-I configuration with the N_3^- anion coordinated *syn*-axial, on the same side as the four methyl groups and fitting into the cavity which they form. This is illustrated in Fig. 2 which also shows the atom-numbering scheme. The most salient structural features relate to the coordination environment of the Co^{II} ion which is intermediate between SPY and TBP. There are two sets of TMC nitrogen donors: N(3), N(5) at a distance of 2·11 Å and N(4), N(8) at an average distance of 2·23 Å. The latter set forms an N—Co—N angle of 167·8°, while the former set bends away strongly from the azide with an N—Co—N angle of 140·8°. The azide ion is in the apical position when the complex is viewed as having distorted SPY geometry, or in the equatorial position when viewed as distorted TBP. The azide ion is approximately linear (176·5°) with a Co—N(6)—N(2) angle of 134·8° and a Co—N(6) distance of 1·974 Å. The azide structural parameters are typical for terminal azide coordination and consistent with those observed in $[Ni(TMC)(N_3)]ClO_4$ (D'Aniello *et al.*, 1975) and $[Ni_2(TMC)_2(N_3)_3]ClO_4$ (Wagner, Mocella, D'Aniello, Wang & Barefield, 1974). While the Co—N distances, both to N_3^- and TMC, are of normal length, the arrangement of the five N donor atoms in $[Co(TMC)(N_3)]^+$ is substantially different from that in the aforementioned Ni^{II} homologue which is square pyramidal with azide in the apical position and the four TMC N atoms coplanar. This structural difference undoubtedly is electronic in origin and related to the *d*-electron configurations: d^7, $S=\frac{3}{2}$ for $[Co(TMC)(N_3)]^+$ and d^8, $S=1$ for $[Ni(TMC)(N_3)]^+$. Although no other crystal structure of $Co(TMC)^{2+}$ adducts has been reported, the structure of $[Fe(TMC)(NO)](BF_4)_2$ is known and germane (Hodges, Wollmann, Kessel, Hendrickson, Van Derveer & Barefield, 1979). This complex is formally d^7, counting the π^* electron from NO, and is remarkably similar in geometry (intermediate SPY, TBP) to that of $[Co(TMC)(N_3)]ClO_4$. While it appears that ligand-field effects can cause the geometry to change substantially from an anticipated

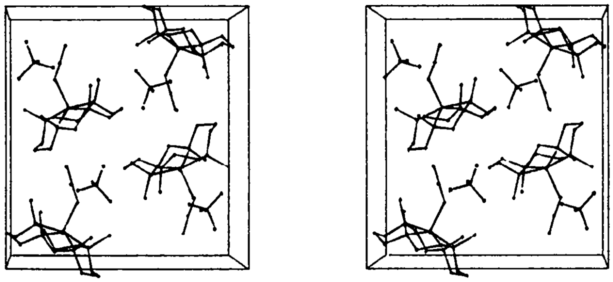

Fig. 1. Stereoscopic view of the unit cell. The *b* axis is horizontal and the *c* axis vertical.

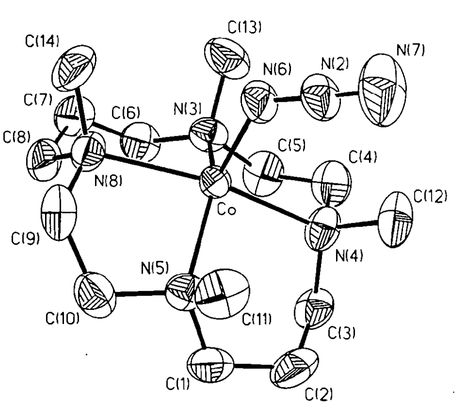

Fig. 2. Illustration of the structure and atom-numbering scheme of $[Co(TMC)(N_3)]ClO_4$. For clarity the H atoms have been omitted.

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Co—N(3)	2·106 (5)	N(4)—C(3)	1·495 (7)
Co—N(4)	2·213 (5)	N(4)—C(4)	1·482 (8)
Co—N(5)	2·130 (5)	N(4)—C(12)	1·489 (7)
Co—N(6)	1·974 (4)	N(5)—C(1)	1·480 (7)
Co—N(8)	2·247 (5)	N(5)—C(10)	1·479 (8)
Cl—O(1)	1·343 (7)	N(5)—C(11)	1·494 (7)
Cl—O(2)	1·446 (6)	N(8)—C(8)	1·485 (7)
Cl—O(3)	1·366 (8)	N(8)—C(9)	1·486 (8)
Cl—O(4)	1·409 (5)	N(8)—C(14)	1·491 (7)
N(2)—N(6)	1·175 (6)	C(1)—C(2)	1·499 (9)
N(2)—N(7)	1·154 (6)	C(2)—C(3)	1·516 (10)
N(3)—C(5)	1·517 (9)	C(4)—C(5)	1·487 (10)
N(3)—C(6)	1·502 (7)	C(6)—C(7)	1·456 (10)
N(3)—C(13)	1·470 (9)	C(7)—C(8)	1·541 (10)
		C(9)—C(10)	1·482 (10)

N(3)—Co—N(4)	84·1 (2)	Co—N(4)—C(12)	115·7 (4)
N(3)—Co—N(5)	140·8 (2)	C(3)—N(4)—C(12)	109·3 (4)
N(4)—Co—N(5)	93·1 (2)	C(4)—N(4)—C(12)	107·4 (5)
N(3)—Co—N(6)	110·7 (2)	Co—N(5)—C(1)	117·0 (4)
N(4)—Co—N(6)	98·6 (2)	Co—N(5)—C(10)	107·2 (4)
N(5)—Co—N(6)	108·4 (2)	C(1)—N(5)—C(10)	107·5 (4)
N(3)—Co—N(8)	92·1 (2)	Co—N(5)—C(11)	107·7 (3)
N(4)—Co—N(8)	167·8 (2)	C(1)—N(5)—C(11)	108·6 (4)
N(5)—Co—N(8)	82·5 (2)	C(10)—N(5)—C(11)	108·5 (5)
N(6)—Co—N(8)	93·6 (2)	Co—N(6)—N(2)	134·8 (4)
O(1)—Cl—O(2)	102·9 (5)	Co—N(8)—C(8)	112·9 (3)
O(1)—Cl—O(3)	117·2 (6)	Co—N(8)—C(9)	103·5 (3)
O(2)—Cl—O(3)	103·2 (5)	C(8)—N(8)—C(9)	109·9 (4)
O(1)—Cl—O(4)	112·4 (5)	Co—N(8)—C(14)	113·8 (4)
O(2)—Cl—O(4)	110·3 (4)	C(8)—N(8)—C(14)	109·4 (4)
O(3)—Cl—O(4)	110·0 (4)	C(9)—N(8)—C(14)	106·9 (5)
N(6)—N(2)—N(7)	176·5 (7)	N(5)—C(1)—C(2)	115·9 (5)
Co—N(3)—C(5)	105·7 (4)	C(1)—C(2)—C(3)	114·6 (5)
Co—N(3)—C(6)	117·5 (4)	N(4)—C(3)—C(2)	114·8 (5)
C(5)—N(3)—C(6)	107·4 (5)	N(4)—C(4)—C(5)	110·8 (5)
Co—N(3)—C(13)	108·6 (4)	N(3)—C(5)—C(4)	110·6 (5)
C(5)—N(3)—C(13)	109·0 (5)	N(3)—C(6)—C(7)	117·1 (5)
C(6)—N(3)—C(13)	108·5 (4)	C(6)—C(7)—C(8)	115·0 (5)
Co—N(4)—C(3)	111·4 (4)	N(8)—C(8)—C(7)	115·3 (5)
Co—N(4)—C(4)	103·5 (3)	N(8)—C(9)—C(10)	111·2 (5)
C(3)—N(4)—C(4)	109·2 (5)	N(5)—C(10)—C(9)	111·8 (5)

square-pyramidal conformation, no unusual bond distances or angles indicative of strain are apparent within the TMC macrocycle as a consequence of its coordination to Co^{II}.

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Acta Cryst. (1989). C**45**, 1697–1699

Structure of Dichlorobis(trimethylphosphine oxide)cobalt(II)

BY MARIE-JOËLLE MENU, MICHEL SIMARD AND ANDRÉ L. BEAUCHAMP

Département de Chimie, Université de Montréal, CP 6128, *Succ. A, Montréal, Québec, H3C 3J7, Canada*

HERBERT KÖNIG, MICHÈLE DARTIGUENAVE AND YVES DARTIGUENAVE

Laboratoire de Chimie de Coordination, 205 *route de Narbonne,* 31077-*Toulouse, France*

AND HANS-FRIEDRICH KLEIN

Anorganische Chemie I, *Technische Hochschule, Darmstadt, Federal Republic of Germany*

(*Received* 3 *February* 1989; *accepted* 15 *March* 1989)

Abstract. $[CoCl_2(C_3H_9OP)_2]$, M_r = 313·99, orthorhombic, $P2_12_12_1$, a = 10·660 (4), b = 11·187 (6), c = 11·807 (3) Å, V = 1408·0 Å^3, Z = 4, D_x = 1·481 Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, μ = 15·64 mm^{-1}, $F(000)$ = 644, T = 170 K, final R = 0·057 for 2149 unique observed reflections. Co has a slightly distorted tetrahedral coordination [Cl—Co—Cl 113·6 (1), O—Co—O 105·6 (2)°] and forms normal Co—Cl [2·262 (2) Å] and Co—O [1·971 (5) Å av.] distances.

Introduction. Dichlorobis(tertiary phosphine oxide)-cobalt(II) complexes have been known for some time (Hunter, Langford, Rodley & Wilkins, 1968; De Bolster, Boutkan, van der Knaap, van Zweeden, Kortram & Groeneveld, 1978; Schmidt & Yoke, 1971), but they still raise interest because cobalt acts as a catalyst in phosphine oxidation (Yamamoto, 1986). On the basis of X-ray diffraction studies, the triphenylphosphine oxide and tribenzylphosphine oxide complexes have been described as tetrahedral four-coordinate Co^{II} complexes (Mangion, Smith & Shore, 1976; De Almeida Santos & Mascarenhas, 1979). The present $CoCl_2(OPMe_3)_2$ compound formed as a by-product of the slow reaction of $CoCl(PMe_3)_3$ with CO_2 and of $CoCl(Ph_2C_2O)(PMe_3)_3$ with H_2, because traces of oxygen were present (König & Klein, 1989). It crystallized out in a pure state from the benzene solution as deep-blue, air-stable crystals. Increasing the amount of O_2 gave rise to untractable mixtures from which only trimethylphosphine oxide could be separated and characterized. The $CoCl_2(OPMe_3)_2$ complex is more conveniently synthesized by reacting $OPMe_3$ with $CoCl_2$ (Hunter *et al.*, 1968; De Bolster *et al.*, 1978; Schmidt & Yoke, 1971).

Experimental. Crystal, 0·065 × 0·11 × 0·19 mm, cut from a large fragment. Enraf–Nonius CAD-4 diffractometer, Niggli matrix of reduced cell indicative of orthorhombic primitive lattice, Laue symmetry and cell dimensions checked with oscillation photographs. Refined cell parameters from 25 centered reflections ($20 < \theta < 25°$), space group $P2_12_12_1$, systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$) identified in full data set. Intensity data collected by ω-scan technique, width = $(1·00 + 0·14 \tan\theta)°$, scan speed 4° min^{-1}, graphite-monochromatized Cu $K\bar{\alpha}$ radiation, $2\theta_{\max}$ = 140°, one asymmetric unit ($+h+k+l$ and $-h+k+l$ octants) measured.

0108-2701/89/111697-03$03.00