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Structure of the Stable Isomer of the (Ethane-1,2-diamine)bis(*N*-methylethane-1,2-diamine)cobalt(III) Cation, *cis*-CH_3,*trans*-NH_2-$[Co(meen)_2(en)]^{3+}$

By Graeme H. Searle and Edward R. T. Tiekink

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, South Australia 5001, *Australia*

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Abstract. (Ethylenediamine)bis(*N*-methylethylenediamine)cobalt(III) dichloride perchlorate monohydrate, $[Co(C_3H_{10}N_2)_2(C_2H_8N_2)](ClO_4)Cl_2.H_2O$, $M_r = 455{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}495(1)$, $b = 14{\cdot}064(1)$, $c = 31{\cdot}121(6)$ Å, $U = 3718(1)$ Å^3, $D_m = 1{\cdot}62$, $D_x = 1{\cdot}628$ Mg m^{-3} for $Z = 8$, Mo $K\bar{\alpha}$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}329$ mm^{-1}, $F(000) = 1800$, $T = 293(2)$ K, $R = 0{\cdot}035$ for 3055 observed reflections. Of three isomers isolated of $[Co(meen)_2(en)]^{3+}$ (meen = *N*-methylethane-1,2-diamine), this is the most stable (85% of total) and elutes last in SP-Sephadex/Na_3PO_4 chromatography. The two cations in the crystallographic asymmetric unit correspond to a single diastereoisomer (in respect of the absolute configurations at the secondary amine centres) of the one geometry *cis*-CH_3,*trans*-NH_2. Cation (1) is *Δ-S,S-λλ(δ)-lel,lel(ob)-eq,eq,* and cation (2) is *Λ-R,R-δδ(δ)-lel,lel(lel)-eq,eq*. These cations are pseudo-enantiomeric, differing in the *ob* (oblique) or *lel* (parallel) orientations of the en ring.

Introduction. In a recent study of cobalt(III) complexes of *N*-methylethane-1,2-diamine (meen), several isomers of each of the complexes $[Co(meen)_3]^{3+}$, $[Co(meen)_2(en)]^{3+}$ and $[Co(meen)(en)_2]^{3+}$ were separated and characterized (Searle & Keene, 1989).

For the (ethane-1,2-diamine)bis(*N*-methylethane-1,2-diamine)cobalt(III) cation $[Co(meen)_2(en)]^{3+}$ prepared under equilibrium conditions (charcoal) three yellow isomers were evident on SP-Sephadex chromatography (with Na_3PO_4) of the preparative mixture {after removal by fractional crystallization of a more soluble red fraction containing $[Co(meen)_3]^{3+}$ complexes}. These three isomers were designated (F), (G) and (H), and they eluted down Sephadex with (F) and (G) together in one band, followed by the major isomer (H). ^{13}C NMR spectra showed that (F) and (H) were each of C_2 symmetry while the spectrum of the minor isomer (G) was consistent with C_1 symmetry. Their approximate equilibrium ratios are (F):(G):(H) = 5:1:36 (Searle & Keene, 1989).

Three geometries are possible for $[Co(meen)_2(en)]^{3+}$ arising from the relative dispositions of the methyl groups, and the NH_2 groups, of the two meen ligands. Also, for each geometry three or four diastereoisomers are possible depending on the absolute configurations *R* or *S* at the two coordinated secondary amine centres (for a particular absolute configuration about the metal). Thus there are ten diastereoisomers in all, and various ring conformational arrangements are possible for each of these. It was deduced that complexes (F), (G) and (H) correspond to the three geometries, since they do not isomerize in base. Also, they are each single diastereoisomers, as shown by ^{13}C NMR spectroscopy.

The crystal structure of isomer (F) was reported previously (Searle & Tiekink, 1989), and it has the molecular structure *trans*-CH_3,*cis*-NH_2-*Λ-RR-δδ(δ)-lel,lel(lel)-eq,eq*. In this and the structure descriptions that follow, brackets are used to distinguish the stereochemical parameters of the en ring. *lel*/*ob* denote the approximately parallel or oblique disposition of the C—C bond of an en-type chelate ring to the pseudo-C_3 axis of the cation, and *eq*/*ax* denote the equatorial or axial disposition of a methyl substituent.

With the (F) structure known, (H) then could be assigned from the ^{13}C NMR spectra, as one of the C_2 diastereoisomers of the *cis*-CH_3,*trans*-NH_2 geometry, leaving (G) as one of the four diastereoisomers (all of C_1 symmetry) of the *cis*-CH_3,*cis*-NH_2 geometry.

A major aim of this work on the cobalt(III) complexes with meen and en has been to provide and characterize a comprehensive system of different complexes and isomers for testing the capability of energy minimization calculative methods to predict and account for the relative stabilities of isomers (as determined by solution equilibrium proportions) and the detailed molecular structures (as determined by crystallographic methods). Thus the present structure determination of isomer (H) was essential to confirm

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Table 1. *Fractional atomic coordinates and B_{eq} values* (Å^2)

$$B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3.$$

	x	*y*	*z*	B_{eq}
Co(1)	0·00081 (14)	−0·05592 (5)	−0·59996 (2)	1·71
Co(2)	−0·00976 (13)	0·08997 (5)	−0·34903 (3)	1·57
N(11)	0·1399 (8)	−0·0670 (5)	−0·6507 (2)	2·92
N(12)	−0·1455 (8)	0·0104 (4)	−0·6390 (2)	2·41
N(13)	−0·1071 (7)	−0·1778 (4)	−0.6118 (2)	2·61
N(14)	−0·1521 (7)	−0·0445 (4)	−0·5515 (2)	2·29
N(15)	0·1082 (8)	0·0633 (4)	−0·5844 (2)	2·37
N(16)	0·1598 (7)	−0·1179 (4)	−0·5619 (2)	2·22
N(21)	0·1360 (8)	0·0982 (4)	−0·3976 (2)	2·80
N(22)	−0·1492 (7)	0·1675 (4)	−0·3857 (2)	2·28
N(23)	0·0855 (7)	0·2042 (4)	−0·3233 (2)	2·25
N(24)	−0·1584 (7)	0·0964 (4)	−0·2996 (2)	2·07
N(25)	−0·1019 (8)	−0·0277 (4)	−0·3719 (2)	2·55
N(26)	0·1322 (7)	0·0038 (4)	−0·3165 (2)	1·99
C(11)	0·0867 (10)	−0·0009 (6)	−0·6840 (3)	2·68
C(12)	−0·0931 (10)	−0·0051 (7)	−0·6855 (3)	3·21
C(13)	−0·1880 (10)	−0·2074 (6)	−0·5724 (3)	3·14
C(14)	−0·2724 (10)	−0·1194 (6)	−0·5548 (3)	3·08
C(15)	−0·2319 (11)	0·0463 (6)	−0·5437 (3)	3·52
C(16)	0·2036 (11)	0·0504 (6)	−0·5458 (3)	3·09
C(17)	0·2837 (10)	−0·0454 (5)	−0·5518 (3)	3·10
C(18)	0·2376 (11)	−0·2098 (6)	−0·5747 (3)	3·44
C(21)	0·0842 (12)	0·1706 (7)	−0·4295 (3)	3·93
C(22)	−0·0895 (12)	0·1683 (7)	−0·4293 (3)	3·98
C(23)	0·0285 (10)	0·2142 (5)	−0·2788 (2)	2·78
C(24)	−0·1423 (9)	0·1904 (6)	−0·2787 (3)	3·06
C(25)	−0·3313 (8)	0·0739 (6)	−0·3057 (3)	3·55
C(26)	−0·0549 (9)	−0·1090 (5)	−0·3444 (3)	2·97
C(27)	0·1169 (9)	−0·0947 (5)	−0·3347 (3)	2·93
C(28)	0·3017 (9)	0·0295 (6)	−0·3104 (3)	2·72
Cl(1)	−0·5672 (3)	−0·7111 (1)	−0·2216 (1)	3·40
O(11)	−0·6849 (8)	−0·6511 (5)	−0·2387 (2)	5·72
O(12)	−0·5945 (10)	−0·8038 (4)	−0·2360 (3)	7·53
O(13)	−0·4187 (9)	−0·6758 (6)	−0·2366 (3)	8·58
O(14)	−0·5818 (10)	−0·7062 (6)	−0·1763 (2)	8·32
Cl(2)	−0·5052 (3)	−0·5243 (1)	−0·0647 (1)	3·16
O(21)	−0·4086 (11)	−0·4602 (5)	−0·0413 (3)	8·95
O(22)	−0·4282 (18)	−0·5692 (7)	−0·0964 (3)	16·05
O(23)	−0·5660 (14)	−0·5934 (6)	−0·0385 (3)	11·82
O(24)	−0·6130 (14)	−0·4701 (7)	−0·0822 (5)	18·86
Cl(3)	0·0236 (3)	−0·1029 (1)	−0·4638 (1)	3·51
Cl(4)	−0·0669 (3)	−0·6096 (1)	−0·3639 (1)	3·62
Cl(5)	0·4435 (3)	−0·6487 (1)	0·1613 (1)	3·69
Cl(6)	−0·4269 (3)	−0·2439 (1)	−0·1301 (1)	3·94
O(*w*1)	−0·5144 (12)	−0·2625 (5)	−0·0317 (2)	8·28
O(*w*2)	0·0111 (8)	−0·0054 (3)	−0·2271 (1)	3·97

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Co(1)—N(11)	1·979 (6)	Co(2)—N(21)	1·957 (6)
Co(1)—N(12)	1·972 (6)	Co(2)—N(22)	1·974 (6)
Co(1)—N(13)	1·979 (6)	Co(2)—N(23)	1·968 (6)
Co(1)—N(14)	1·988 (6)	Co(2)—N(24)	1·991 (6)
Co(1)—N(15)	1·970 (6)	Co(2)—N(25)	1·964 (6)
Co(1)—N(16)	1·997 (6)	Co(2)—N(26)	1·987 (6)
N(11)—C(11)	1·46 (1)	N(21)—C(21)	1·49 (1)
N(12)—C(12)	1·53 (1)	N(22)—C(22)	1·45 (1)
N(13)—C(13)	1·47 (1)	N(23)—C(23)	1·476 (9)
N(14)—C(14)	1·47 (1)	N(24)—C(24)	1·48 (1)
N(14)—C(15)	1·47 (1)	N(24)—C(25)	1·515 (9)
N(15)—C(16)	1·46 (1)	N(25)—C(26)	1·483 (9)
N(16)—C(17)	1·50 (1)	N(26)—C(27)	1·503 (9)
N(16)—C(18)	1·51 (1)	N(26)—C(28)	1·497 (9)
C(11)—C(12)	1·53 (1)	C(21)—C(22)	1·48 (2)
C(13)—C(14)	1·53 (1)	C(23)—C(24)	1·49 (1)
C(16)—C(17)	1·52 (1)	C(26)—C(27)	1·50 (1)
Cl(1)—O(11)	1·411 (8)	Cl(2)—O(21)	1·42 (1)
Cl(1)—O(12)	1·398 (7)	Cl(2)—O(22)	1·34 (1)
Cl(1)—O(13)	1·433 (9)	Cl(2)—O(23)	1·37 (1)
Cl(1)—O(14)	1·417 (8)	Cl(2)—O(24)	1·31 (1)
N(11)—Co(1)—N(12)	85·5 (3)	N(21)—Co(2)—N(22)	84·3 (3)
N(11)—Co(1)—N(13)	93·4 (3)	N(21)—Co(2)—N(23)	90·3 (3)
N(11)—Co(1)—N(14)	176·1 (3)	N(21)—Co(2)—N(24)	174·0 (3)
N(11)—Co(1)—N(15)	89·2 (3)	N(21)—Co(2)—N(25)	91·3 (3)
N(11)—Co(1)—N(16)	92·0 (3)	N(21)—Co(2)—N(26)	92·6 (3)
N(12)—Co(1)—N(13)	90·2 (3)	N(22)—Co(2)—N(23)	91·8 (2)
N(12)—Co(1)—N(14)	91·0 (3)	N(22)—Co(2)—N(24)	92·4 (2)
N(12)—Co(1)—N(15)	92·3 (3)	N(22)—Co(2)—N(25)	91·0 (2)
N(12)—Co(1)—N(16)	176·4 (3)	N(22)—Co(2)—N(26)	174·9 (2)
N(13)—Co(1)—N(14)	84·8 (2)	N(23)—Co(2)—N(24)	84·8 (2)
N(13)—Co(1)—N(15)	176·5 (2)	N(23)—Co(2)—N(25)	176·9 (2)
N(13)—Co(1)—N(16)	92·6 (2)	N(23)—Co(2)—N(26)	92·4 (2)
N(14)—Co(1)—N(15)	92·7 (2)	N(24)—Co(2)—N(25)	93·7 (2)
N(14)—Co(1)—N(16)	91·5 (3)	N(24)—Co(2)—N(26)	91·1 (2)
N(15)—Co(1)—N(16)	85·0 (2)	N(25)—Co(2)—N(26)	85·0 (2)
Co(1)—N(11)—C(11)	109·3 (5)	Co(2)—N(21)—C(21)	111·6 (5)
Co(1)—N(12)—C(12)	109·4 (5)	Co(2)—N(22)—C(22)	109·7 (5)
Co(1)—N(13)—C(13)	107·8 (5)	Co(2)—N(23)—C(23)	109·0 (4)
Co(1)—N(14)—C(14)	110·0 (5)	Co(2)—N(24)—C(24)	108·8 (4)
Co(1)—N(14)—C(15)	119·7 (5)	Co(2)—N(24)—C(25)	120·6 (5)
Co(1)—N(15)—C(16)	110.7 (5)	Co(2)—N(25)—C(26)	109·5 (5)
Co(1)—N(16)—C(17)	107·6 (4)	Co(2)—N(26)—C(27)	108·5 (4)
Co(1)—N(16)—C(18)	121·0 (5)	Co(2)—N(26)—C(28)	120·1 (4)
C(14)—N(14)—C(15)	108·3 (6)	C(24)—N(24)—C(25)	109·3 (6)
C(17)—N(16)—C(18)	109·3 (6)	C(27)—N(26)—C(28)	110·7 (6)
N(11)—C(11)—C(12)	107·8 (7)	N(21)—C(21)—C(22)	106·1 (7)
N(12)—C(12)—C(11)	104·8 (6)	N(22)—C(22)—C(21)	110·7 (7)
N(13)—C(13)—C(14)	106·9 (6)	N(23)—C(23)—C(24)	107·5 (6)
N(14)—C(14)—C(13)	106·2 (6)	N(24)—C(24)—C(23)	106·8 (6)
N(15)—C(16)—C(17)	104·9 (7)	N(25)—C(26)—C(27)	105·9 (6)
N(16)—C(17)—C(16)	108·3 (7)	N(26)—C(27)—C(26)	106·4 (6)
O(11)—Cl(1)—O(12)	108·6 (5)	O(21)—Cl(2)—O(22)	113·2 (8)
O(11)—Cl(1)—O(13)	107·2 (5)	O(21)—Cl(2)—O(23)	111·4 (6)
O(11)—Cl(1)—O(14)	106·4 (5)	O(21)—Cl(2)—N(24)	104·3 (7)
O(12)—Cl(1)—O(13)	111·4 (6)	O(22)—Cl(2)—O(23)	106·7 (6)
O(12)—Cl(1)—O(14)	110·4 (5)	O(22)—Cl(2)—O(24)	107·9 (9)
O(13)—Cl(1)—O(14)	112·6 (6)	O(23)—Cl(2)—O(24)	113·4 (8)

its geometry, and to ascertain the particular diastereoisomer and the conformational details.

Experimental. The compound [major isomer (H)] was prepared by precipitation from an evaporated HCl solution with $HClO_4$ as described previously (Searle & Keene, 1989). Crystals obtained by slow recrystallization from a 0·1 *M* $HClO_4$ solution by using ethanol vapour diffusion. Density by flotation. Enraf–Nonius CAD-4*F* diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation; ω:2θ scan technique. Cell parameters on crystal 0·68 × 0·18 × 0·18 mm from least-squares procedure on 25 reflections ($9 \leq \theta \leq 15°$). Analytical absorption correction applied; max. and min. transmission factors 0·834 and 0·747 (Sheldrick, 1976). Total of 4914 reflections ($1 \leq \theta \leq 25·0°$) measured in the range $-10 \leq h \leq 3$, $-16 \leq k \leq 0$, $-35 \leq l \leq 0$; some Friedel pairs also included. No significant variation in the net intensities of three reference reflections (3,2,10, 258, 425) measured every 3600 s. 4740 unique reflections ($R_{\rm int}$ 0·031) and 3055 satisfied $I \geq 2·5\sigma(I)$. Structure solved by direct methods (Sheldrick, 1986), blocked-matrix least-squares refinement of 422 parameters based on *F* (Sheldrick, 1976). Anisotropic thermal parameters for non-H atoms and H atoms included at their calculated positions. The absolute structure of the crystal was determined from differences in Friedel pairs included in the data set. At convergence $R = 0·035$, $wR = 0·037$, $w = 4·26/[\sigma^2(F) + 0·0004F^2]$, $S = 3·90$, $(\Delta/\sigma)_{\rm max} \leq 0·001$, $(\Delta\rho)_{\rm max} = 0·88$, $(\Delta\rho)_{\rm min} = -0·52\,{\rm e}\,Å^{-3}$; no extinction correction. Scattering factors for H, C, N, O and Cl given in *SHELX76* (Sheldrick, 1976) and those for Co^{3+} corrected for *f′* and *f″* (Hamilton & Ibers, 1974). All calculations on SUN4/280 computer system. Atomic parameters are given in Table 1, bond distances and angles in Table 2,* and the numbering scheme used is shown in Fig. 1.

Discussion. The crystal structure determination confirms the stoichiometry of isomer (H) as [Co(meen)$_2$(en)](ClO$_4$)Cl$_2$.H$_2$O. The compound crystallizes in the acentric space group $P2_12_12_1$ in which the crystallographic asymmetric unit contains two [Co(meen)$_2$(en)]$^{3+}$ cations [denoted (1) and (2)], two ClO_4^- anions, four Cl^- anions and two water molecules of crystallization, In the cations, the cobalt(III) centres exist in distorted octahedral geometries each defined by six N donor atoms derived from two meen ligands and an en ligand. The Co—NH$_2$ bond distances lie in the range 1·957 (6) to 1·979(6) Å, and the Co—NH(CH$_3$) bond distances are slightly longer as expected and lie in the narrow range 1·987(6) to 1·998(6) Å. The maximum deviation from the ideal octahedral geometry is manifested in the contraction from 90° of the N(13)—Co(1)—N(14) angle to 84·8(2)° for cation (1), and the reduction from 180° for N(21)—Co(2)—N(4) to 174·0 (3)° for cation (2). The N—C and C—C bond parameters are normal. No special features are associated with the two unique perchlorate anions in the structure although we note the high thermal motion of the Cl(2)O$_4$ group. Particularly important to this study is the assignment of the conformational details of the two cations which differ non-trivially from each other.

Both cations are of the one geometry, *cis*-CH$_3$,-*trans*-NH$_2$-[Co(meen)$_2$(en)]$^{3+}$, and their diastereoisomeric and conformational structures are designated as follows:

cation (1): *Δ-S,S-λλ(δ)-lel,lel(ob)-eq,eq*;

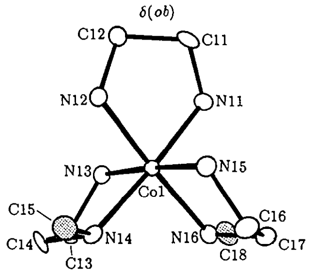
cation (2): *Λ-R,R-δδ(δ)-lel,lel(lel)-eq,eq.*

From the above description, and as seen in Fig. 1, it is evident that the two cations comprising the asymmetric unit are 'pseudo-enantiomeric' with the difference in the two en ring conformations precluding a true enantiomeric relationship between the two cations (aside from crystal packing effects). The en conformations are actually the same in the absolute sense, *δ*, so that they have different geometric relationships *ob* and *lel* in the two cations. Therefore crystals of isomer (H) can be regarded as being examples of the less common occurrence of spontaneous resolution (Searle & Tiekink, 1989) even though both the *Δ* and *Λ* optical isomers are present in the crystal; the net asymmetry resides only in the en conformations. Crystals of the opposite chirality to that selected for the present analysis would contain two cations with the chiroptical/conformational designations *Λ-R,R-δδ(λ)-lel,lel(ob)-eq,eq* and *Δ-S,S-λλ(λ)-lel,lel(lel)-eq,eq*.

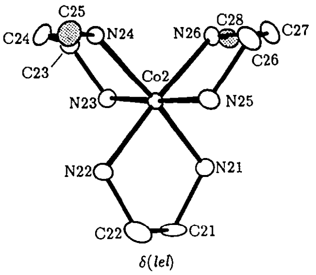
No evidence was found for the existence of other kinds of crystals, containing the following pairs of 'pseudo-enantiomeric' cations: *ΔS,S-λλ(λ)-lel,lel-(lel)-eq,eq/Λ-R,R-δδ(δ)-lel,lel(lel)-eq,eq* and *ΔS,S-λλ(δ)-lel,lel(ob)-eq,eq/Λ-R,R-δδ(λ)-lel,lel(ob)-eq,eq.* In these the two cations would have the en rings either both *lel* or both *ob*, so that it seems that crystal forces favour the mixed en conformation arrangement.

As noted earlier the ^{13}C NMR spectrum of isomer (H) was consistent with the cation having C_2 symmetry. In the solid state the fixed conformations of the en rings preclude C_2 symmetry for each cation (there is pseudo twofold symmetry only). However, in solution conformations of unhindered saturated chelate rings interconvert rapidly, so that the en ring conformations would be averaged and the cations would have effective C_2 symmetry. As a consequence there are four equal resonances in the ^{13}C NMR spectrum of (H).

A point of fundamental interest concerns the predominance of certain stereochemical features in these structures. In both cations of (H), the meen ring



Cation (1)



Cation (2)

Fig. 1. Numbering scheme for *cis*-CH$_3$,*trans*-NH$_2$-[Co(meen)$_2$(en)]$^{3+}$, major isomer (H), with methyl C atoms shaded. The pseudo-enantiomeric cations designated (1) and (2) in the asymmetric unit are: cation (1), *Δ-S,S-λλ(δ)-lel,lel(ob)-eq,eq*; and cation 2, *Λ-R,R-δδ(δ)-lel,lel(lel)-eq,eq.* Diagram drawn with 25% probability ellipsoids (Johnson, 1971).

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* Lists of structure factors, thermal parameters, H-atom parameters and hydrogen-bonding contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51887 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

geometries involve equatorial methyl substituents and *lel* conformations, just as was found in the structure of isomer (F) (Searle & Tiekink, 1989). These stereochemical arrangements generally give lower-energy structures in cobalt(III) complexes with pn, meen and en (pn is propane-1,2-diamine), although some instances of axial methyls and *ob* conformations have been found in $[Co(meen)_3]^{3+}$ complexes (Searle & Tiekink, 1989).

There are several significant interionic contacts in the crystal lattice arising from numerous potential hydrogen-bonding sites and a brief description of these follows. The perchlorate group with Cl(1) makes close contact with the amine groups $N(11)H_2$ and $N(13)H_2$ of cation (1). The second perchlorate makes three contacts with amines $N(21)H_2$, $N(22)H_2$ and $N(25)H_2$ of cation (2) and makes a fourth contact with a solvent water molecule, $H_2O(w1)$. The chlorides Cl(1), Cl(2), Cl(3) and Cl(4) make three, four, two and two contacts respectively in the lattice. The two solvent water molecules are involved in four and two significant contacts respectively.

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Structure of Hydrogen Bis(2-methyl-8-quinolinolato)dioxovanadate(V)

BY NORIYUKI NAKASUKA* AND MOTOHARU TANAKA

Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University,
Chikusa, Nagoya 464-01, *Japan*

AND MOTOO SHIRO

Shionogi Research Laboratories, Shionogi & Co. Ltd, Fukushima, Osaka 553, *Japan*

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Abstract. $H[V(C_{10}H_8NO)_2O_2].3H_2O$, $M_r = 454{\cdot}4$, monoclinic, $P2_1/c$, $a = 8{\cdot}544\,(1)$, $b = 22{\cdot}401\,(2)$, $c = 11{\cdot}488\,(1)$ Å, $\beta = 109{\cdot}95\,(1)°$, $V = 2066{\cdot}7\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}470$, $D_x = 1{\cdot}460$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 46{\cdot}5$ cm^{-1}, $F(000) = 944$, $T = 298$ K, $R = 0{\cdot}068$ for 2823 observed reflections. The title compound is yellowish and has a monomeric structure, in contrast with the dimeric structure of μ-oxo-bis[oxobis(8-quinolinolato)vanadium(V)], which is black in color. The V atom is in a five-coordinate distorted trigonal-bipyramidal environment, where two vanadyl O atoms and an O atom from the chelating ligand define the equatorial plane. The N atom of the other methylquinolinol is not coordinated toV^V but protonated.

Introduction. The black color of vanadium(V) 8-quinolinolate has been considered a mysterious phenomenon, since most other metal complexes of this ligand are yellow in color except for the black iron(III) complex (Borrel & Pâris, 1950; Bielig & Bayer, 1953; Hollingshead, 1956). This question was clearly resolved by X-ray crystallography demonstrating that the vanadium(V) complex is an oxo-bridged dimer (Yamada, Katayama, Tanaka & Tanaka, 1984), which is quite consistent with the presence of dimeric species in non-aqueous solutions as proved by the solvent extraction technique (Yuchi, Yamada & Tanaka, 1980). Methyl substitution at the 2-position, however, leads to a yellowish vanadium(V) compound, which is quite sparingly soluble in both aqueous and non-aqueous solvents. The present study aims to determine the structure of the 2-methyl-8-quinolinolate complex and to explain the different colors of these homologs.

Experimental. Yellowish transparent crystals grown from an acetone solution containing only a little

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* To whom correspondence should be addressed.