that they form $[Nb_6O_{24}]$ units. These units are stacked along the c axis and share corners in order to form $[Nb_6O_{21}]_\infty$ columns. The columns are linked together by sharing their vacant corners with single NbO_6 octahedra [Nb(1) type]. This framework delimits cages where the K ions are located. The structure may also be described as $[Nb_8O_{24}]_{2\infty}$ layers stacked along c and sharing their free corners.

The spread of the Nb(2)—O distances is half that observed from powder data but it is confirmed that the $Nb(2)O_6$ octahedron is strongly distorted as shown by the wide range of O—Nb(2)—O angles (75.4 to 99.2°) and O—O distances (2.559 to 3.182 Å) (Table 2). The Nb(1)O$_6$ octahedra are more regular. The mean valency of the Nb atoms deduced from the Zachariasen (1978) curve suggests that the Nb(1) sites are mainly occupied by Nb^V (mean valency 4.94), whereas the electrons would be preferentially delocalized in the Nb(2)O$_6$ octahedra (mean valency 4.86) in agreement with the size of these two types of sites. The mean valency deduced from this calcula-

tion (4.88) is in agreement with the valency deduced from the charge balance according to the formula $K_3Nb_7^VNb^{IV}O_{21}$ (4.875).

The K ions lie in cages between the $[Nb_8O_{24}]_{2\infty}$ layers. They are surrounded by 12 O atoms whose distances are smaller than 3.25 Å.

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Seven-Coordinate Manganese(II) Complexes of 2,6-Bis[1-(2-hydroxyethylimino)ethyl]pyridine

BY SALLY BROOKER AND VICKIE MCKEE*

Chemistry Department, University of Canterbury, Christchurch, New Zealand

Abstract. Diaqua{2,6-bis[1-(2-hydroxyethylimino)-ethyl]pyridine-N,N',N'',O,O'}manganese(II) diperchlorate, [Mn(L)(H$_2$O)$_2$](ClO$_4$)$_2$ (L = C$_{13}$H$_{19}$N$_3$O$_2$) (I), M_r = 539.2, monoclinic, $C2/c$, a = 16.142 (3), b = 12.222 (3), c = 11.047 (3) Å, β = 94.41 (2)°, V = 2173 (1) Å^3, Z = 4, D_x = 1.648 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.893 mm^{-1}, F(000) = 1108, T = 293 K, final R = 0.064 for 1684 [$F > 6\sigma(F)$] independent observed reflections. {2,6-Bis[1-(2-hydroxyethylimino)ethyl]pyridine-N,N',N'',O,O'}bis(thiocyanato-N)manganese(II), [Mn(L)(NCS)$_2$] (II), M_r = 420, monoclinic, $I2/a$, a = 9.902 (2), b = 12.581 (2), c = 15.203 (3) Å, β = 101.46 (2)°, V = 1856.2 (6) Å^3, Z = 4, D_x = 1.504 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.917 mm^{-1}, F(000) = 868, T = 293 K, final R = 0.043 for 1505 [$F > 6\sigma(F)$] independent observed reflections. Bisazido{2,6-bis[1-(2-hydroxyethyl-imino)ethyl]pyridine-N,N',N'',O,O'}manganese(II), [Mn(L)(N$_3$)$_2$] (III), M_r = 388, orthorhombic, $Pbcn$, a = 18.643 (7), b = 12.616 (3), c = 7.127 (3) Å, V = 1676 (1) Å^3, Z = 4, D_x = 1.539 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.783 mm^{-1}, F(000) = 804, T = 173 K, final R = 0.041 for 818 [$F > 6\sigma(F)$] independent observed reflections. In each structure the Mn coordination geometry is approximately pentagonal bipyramidal with the five donors from the ligand L occupying the pentagonal plane. There is extensive hydrogen bonding in each structure.

Introduction. Many seven-coordinate complexes of first-row transition metals have been synthesized using macrocyclic ligands (Nelson, 1980; Drew, Othman & Nelson, 1976; Drew, Othman, McFall, McIlroy & Nelson, 1977) or rigid, resonance-stabilized planar systems (Capparelli, de Meester, Goodgame, Gunn & Skapski, 1985; Pelizzi, Pelizzi,

Predieri & Resola, 1982) to enforce pentagonal planar coordination. The ligand 2,6-bis[1-(2-hydroxyethylimino)ethyl]pyridine (L) is neither macrocyclic nor rigid; it can adopt a conformation in which it acts as a planar pentadentate ligand but this geometry is not enforced by either of the above mechanisms. We recently reported a series of Ni complexes of L in which the structure obtained was shown to depend on the nature of the counter ion, although, in every case, the Ni atoms were six-coordinate (Brooker & McKee, 1990b). A series of manganese(II) complexes was also synthesized and the structure of [Mn(L)Cl$_2$] reported (Brooker & McKee, 1990a). In contrast to the Ni series, the Mn complex was seven-coordinate. In this paper we report the structures of the remaining members of this series, all of which are seven-coordinate pentagonal bipyramidal complexes.

(L)
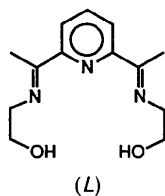
Experimental. The three yellow complexes were prepared as reported previously (Brooker & McKee, 1990a). Data sets were collected using ω scans on a Nicolet R3m four-circle diffractometer, using graphite-monochromated Mo Kα radiation. Crystal stability was monitored by recording three standards every 97 reflections and no significant variations were observed. Each data set was corrected for Lorentz and polarization effects and empirical absorption corrections, based on ψ-scan data, were applied. Details of the experimental data for each complex are recorded in Table 1. Systematic absences led to space group assignments of C2/c (No. 15) for (I), I2/a (a non-standard setting of No. 15) for (II), and Pbcn (No. 60) for (III). Structures (I) and (II) were solved using Patterson techniques to locate the heavier atoms; (III) was solved by direct methods, which revealed most of the structure. In each case the remaining non-H atoms were located using difference Fourier maps and refined on F by full-matrix least-squares techniques. The perchlorate anion in (I) shows some disorder and this has been modelled as a rotation about the Cl—O(14) bond. Site-occupancy factors were set at 0.70 for O(11), O(12) and O(13) and at 0.30 for O(15), O(16) and O(17). Anisotropic thermal parameters were assigned to all the non-H atoms of each structure, except for the minor component of the disordered perchlorate anion in (I). H atoms were inserted at calculated positions with common fixed thermal parameters.

Table 1. *Experimental details*

	(I)	(II)	(III)
Crystal size (mm)	0.53 × 0.41 × 0.16	0.64 × 0.41 × 0.31	0.4 × 0.28 × 0.16
No. and 2θ range (°) of reflections used to determine cell parameters	24, $5 < 2\theta < 34$	25, $5 < 2\theta < 36$	25, $6 < 2\theta < 32$
Data collection 2θ range (°)	$4 < 2\theta < 50$	$4 < 2\theta < 50$	$4 < 2\theta < 50$
Data collection hkl range	$-19 \leq h \leq 19$	$-11 \leq h \leq 11$	$0 \leq h \leq 22$
	$0 \leq k \leq 14$	$0 \leq k \leq 14$	$0 \leq k \leq 14$
	$0 \leq l \leq 13$	$0 \leq l \leq 18$	$0 \leq l \leq 8$
Scan width (°)	1.6	1.6	1.4
Scan rate (° min^{-1})	3.91	2.93	4.88
No. of reflections collected	2088	2503	1736
No. of unique reflections	1914	1638	1736
No. of reflections with $F > 6\sigma(F)$	1684	1505	818
R_{int}	0.0144	0.0063	–
Standard reflections	600, 060, 004	600, 060, 006	400, 020, 002
Maximum, minimum transmission factors	0.757, 0.526	0.841, 0.766	0.820, 0.775
No. of parameters refined	154	115	115
R	0.0644	0.0448	0.0410
wR	0.1021	0.0782	0.0506
S	2.13	1.68	1.04
w in weighting scheme	0.0018	0.0017	0.001
Maximum, mean shift/e.s.d	0.019, 0.002	0.019, 0.005	0.002, 0.001
Maximum, minimum peaks in final difference Fourier map (e Å^{-3})	0.43, −0.64	0.36, −0.65	0.31, −0.34

Atomic coordinates are listed in Table 2 and selected bond lengths and angles are given in Table 3.* The programs and atomic scattering factors used are contained in the *SHELXTL-PC* package (Sheldrick, 1989).

Discussion. The structures of [Mn(L)(H$_2$O)$_2$]$^{2+}$, [Mn(L)(NCS)$_2$] and [Mn(L)(N$_3$)$_2$] are shown in Figs. 1, 2 and 3, respectively. In contrast to the related Ni complexes (Brooker & McKee, 1990b), these structures are quite similar to each other and to the previously published [Mn(L)Cl$_2$] complex (IV) (Brooker & McKee, 1990a). In each of the present complexes [but not in (IV)], the atoms Mn, N(1) and C(3) lie on a crystallographic twofold axis so that the asymmetric unit contains half the complex. The Mn atom and the five donors from L are approximately coplanar; the sums of the angles about Mn are 362.1 (I), 360.1 (II) and 361.3° (III). The Mn coordination spheres are completed by two axial ligands resulting in approximately pentagonal bipyramidal geometry. The coordinated thiocyanate and azide ligands are, as expected, close to linear [N(20)—C(21)—S(22) 179.0 (3) and N(20)—N(21)—N(22) 179.6 (5)°]. They are considerably tilted, in different directions, relative to the Mn—N(20) bond [Mn—N(20)—C(21) 150.5 (3), Mn—N(20)—N(21) 123.5 (4)°]. These differences seem largely to result from the packing and hydrogen-bonding requirements which are dis-

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55569 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0301]

Table 2. *Atomic coordinates* (× 10⁴) *and equivalent isotropic displacement coefficients* (Å² × 10³)

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

	x	y	z	U_{eq}
Compound (I)				
Mn	5000	7575 (1)	7500	39 (1)
N(1)	5000	5718 (4)	7500	44 (1)
C(3)	5000	3495 (6)	7500	82 (3)
C(4)	4504 (4)	4034 (4)	8249 (5)	72 (2)
C(5)	4531 (3)	5180 (4)	8242 (4)	52 (1)
C(6)	4054 (3)	5896 (4)	9052 (4)	53 (1)
C(7)	3463 (3)	5375 (5)	9847 (5)	75 (2)
N(2)	4195 (2)	6915 (3)	8952 (3)	49 (1)
C(8)	3778 (3)	7742 (5)	9644 (5)	66 (2)
C(9)	4333 (4)	8732 (5)	9772 (5)	71 (2)
O(1)	4644 (2)	9006 (3)	8649 (3)	62 (1)
O(2)	6162 (2)	7628 (3)	8700 (4)	76 (1)
Cl	1883 (1)	6179 (1)	6911 (1)	57 (1)
O(11)	2297 (8)	5164 (8)	7186 (8)	147 (5)
O(15)	2661 (15)	5973 (19)	6735 (21)	125 (7)
O(12)	1865 (7)	6137 (9)	5645 (7)	145 (5)
O(16)	1262 (17)	6496 (19)	6050 (22)	134 (7)
O(13)	1098 (6)	6022 (8)	7292 (11)	137 (4)
O(17)	1644 (16)	5370 (19)	7708 (20)	118 (6)
O(14)	2186 (6)	7095 (8)	7513 (9)	176 (4)
Compound (II)				
Mn	2500	7711 (1)	0	37 (1)
N(1)	2500	5886 (2)	0	32 (1)
C(3)	2500	3702 (3)	0	56 (2)
C(4)	1857 (3)	4248 (2)	584 (2)	50 (1)
C(5)	1877 (2)	5351 (2)	567 (2)	35 (1)
C(6)	1216 (2)	6042 (2)	1168 (2)	38 (1)
C(7)	536 (4)	5517 (3)	1858 (2)	61 (1)
N(2)	1289 (2)	7034 (2)	1039 (1)	38 (1)
C(8)	705 (3)	7820 (3)	1582 (2)	54 (1)
C(9)	409 (3)	8820 (2)	1043 (3)	60 (1)
O(1)	1576 (3)	9102 (2)	683 (2)	90 (1)
N(20)	4428 (3)	7817 (3)	1017 (2)	61 (1)
C(21)	5525 (3)	8156 (2)	1259 (2)	43 (1)
S(22)	7073 (1)	8611 (1)	1601 (1)	58 (1)
Compound (III)				
Mn	5000	1795 (1)	2500	26 (1)
N(1)	5000	3620 (4)	2500	24 (2)
C(3)	5000	5803 (5)	2500	38 (2)
C(4)	4385 (4)	5254 (4)	2015 (7)	33 (2)
C(5)	4413 (3)	4149 (4)	2028 (7)	27 (2)
C(6)	3787 (3)	3460 (4)	1491 (7)	30 (2)
C(7)	3074 (3)	3965 (4)	1119 (10)	49 (2)
N(2)	3924 (2)	2475 (3)	1433 (6)	31 (1)
C(8)	3370 (3)	1694 (4)	1008 (8)	41 (2)
C(9)	3735 (3)	748 (4)	160 (9)	45 (2)
O(1)	4305 (2)	424 (2)	1380 (5)	35 (1)
N(20)	5539 (2)	1688 (3)	− 272 (6)	33 (1)
N(21)	6064 (3)	2182 (3)	− 674 (7)	35 (2)
N(22)	6577 (2)	2660 (4)	− 1056 (8)	52 (2)

Table 3. *Selected bond lengths* (Å) *and angles* (°)

Compound (I)

Mn—N(1)	2.269 (5)	Mn—N(2)	2.287 (4)
Mn—O(1)	2.262 (4)	Mn—O(2)	2.213 (4)
Mn—N(2')	2.287 (4)	Mn—O(1')	2.262 (4)
Mn—O(2')	2.213 (4)		

N(1)—Mn—N(2)	69.4 (1)	N(1)—Mn—O(1)	140.7 (1)
N(2)—Mn—O(1)	72.3 (1)	N(1)—Mn—O(2)	91.7 (1)
N(2)—Mn—O(2)	95.3 (1)	O(1)—Mn—O(2)	83.2 (1)
N(1)—Mn—N(2')	69.4 (1)	N(2)—Mn—N(2')	138.7 (2)
O(1)—Mn—N(2')	148.1 (1)	O(2)—Mn—N(2')	85.9 (1)
N(1)—Mn—O(1')	140.7 (1)	N(2)—Mn—O(1')	148.1 (1)
O(1)—Mn—O(1')	78.7 (2)	O(2)—Mn—O(1')	94.2 (1)
N(1)—Mn—O(2')	91.7 (1)	N(2)—Mn—O(2')	85.9 (1)
O(1)—Mn—O(2')	94.2 (1)	O(2)—Mn—O(2')	176.6 (2)

Compound (II)

Mn—N(1)	2.296 (3)	Mn—N(2)	2.326 (2)
Mn—O(1)	2.314 (3)	Mn—N(20)	2.209 (3)
Mn—N(2')	2.326 (2)	Mn—O(1')	2.314 (3)
Mn—N(20')	2.209 (3)		

N(1)—Mn—N(2)	68.5 (1)	N(1)—Mn—O(1)	139.1 (1)
N(2)—Mn—O(1)	70.7 (1)	N(1)—Mn—N(20)	93.4 (1)
N(2)—Mn—N(20)	92.1 (1)	O(1)—Mn—N(20)	90.2 (1)
N(1)—Mn—N(2')	68.5 (1)	N(2)—Mn—N(2')	137.1 (1)
O(1)—Mn—N(2')	152.2 (1)	N(20)—Mn—N(2')	90.4 (1)
N(1)—Mn—O(1')	139.1 (1)	N(2)—Mn—O(1')	152.2 (1)
O(1)—Mn—O(1')	81.7 (2)	N(20)—Mn—O(1')	84.5 (1)
N(1)—Mn—N(20')	93.4 (1)	N(2)—Mn—N(20')	90.4 (1)
O(1)—Mn—N(20')	84.5 (1)	N(20)—Mn—N(20')	173.1 (2)

Compound (III)

Mn—N(1)	2.302 (5)	Mn—N(2)	2.311 (4)
Mn—O(1)	2.304 (3)	Mn—N(20)	2.221 (4)
Mn—N(2')	2.311 (4)	Mn—O(1')	2.304 (3)
Mn—N(20')	2.221 (4)		

N(1)—Mn—N(2)	68.2 (1)	N(1)—Mn—O(1)	138.7 (1)
N(2)—Mn—O(1)	71.1 (1)	N(1)—Mn—N(20)	93.5 (1)
N(2)—Mn—N(20)	97.1 (2)	O(1)—Mn—N(20)	84.3 (1)
N(1)—Mn—N(2')	68.2 (1)	N(2)—Mn—N(2')	136.4 (2)
O(1)—Mn—N(2')	151.8 (1)	N(20)—Mn—N(2')	85.5 (2)
N(1)—Mn—O(1')	138.7 (1)	N(2)—Mn—O(1')	151.8 (1)
O(1)—Mn—O(1')	82.7 (2)	N(20)—Mn—O(1')	90.5 (1)
N(1)—Mn—N(20')	93.5 (1)	N(2)—Mn—N(20')	85.5 (2)
O(1)—Mn—N(20')	90.5 (1)	N(20)—Mn—N(20')	173.1 (2)

cussed below. Bond lengths and angles within the complexes are unremarkable.

In all three complexes the packing is determined by hydrogen bonding and, since this involves the axial ligands and, for (I), the perchlorate anion, the arrangement is different in each case. Complex (I) is the most complicated owing to the disorder of the perchlorate anion. Packing diagrams for the major and minor occupancy sites are shown in Figs. 4 and 5, respectively. In the major orientation, the perchlorate anion is hydrogen bonded to the alcohol group of one cation [O(13)···O(1) 2.90 (1) Å] and to the axial water ligand of a second cation [O(12)···O(2) 2.79 (1) Å]. In the minor configuration, the axial water ligands on adjacent cations are bridged by two

perchlorate ions [O(2)···O(15) 2.84 (1), O(2)···O(16) 2.80 (1) Å].

Fig. 6 shows a packing diagram for (II). The alcohol O atoms of L are hydrogen bonded to the thiocyanate S atoms of neighbouring molecules [O(1)···S(22) 3.19 (1) Å]. In (III), the hydrogen bonding is between the alcohol and azide groups [O(1)···N(20) 2.79 (1) Å; Fig. 7]. In contrast to the thiocyanate complex, it is the azide N atom bound to Mn which is involved in the hydrogen bonding rather than the terminal N atom. In both the thiocyanate and azide complexes the hydrogen bonding results in chains lying along the x axis.

These structures demonstrate that the structural requirements for seven-coordination are relaxed somewhat for a d^5 ion, such as Mn^II, with no stereochemical preferences. In these complexes, the geometry is defined by the rigidity and small bite angle (mean 68.7°) of the pyridinediimine unit. Three donors, constrained within an arc of approximately 137°, and coplanar with the Mn, leave ample space for two more donors in the same plane. The N(2)—C(8)—C(9)—O(1) link also has a small bite angle

(mean 71.4°), close to the ideal of 72° for a pentagonal plane. Extending this saturated chain by one extra C atom disrupts the seven-coordinate geometry and, with thiocyanate counter ions, leads to a polymeric structure containing six-coordinate Mn (Brooker & McKee, 1990a).
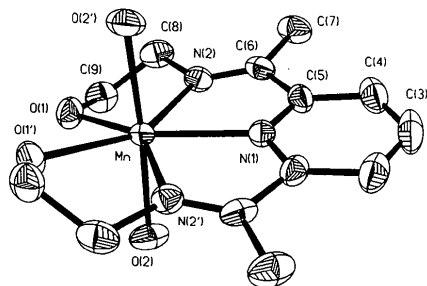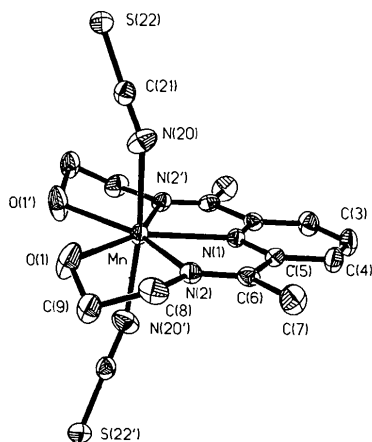

Fig. 1. Perspective view of [Mn(L)(H$_2$O)$_2$]$^{2+}$, (I).
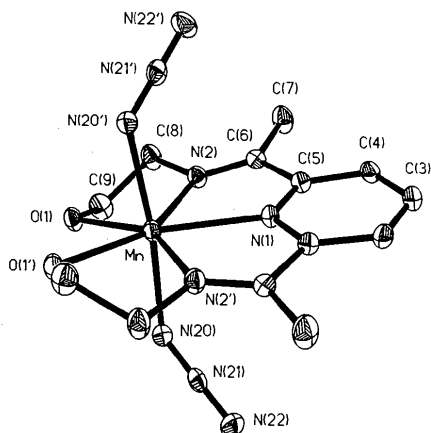

Fig. 2. Perspective view of [Mn(L)(NCS)$_2$], (II).
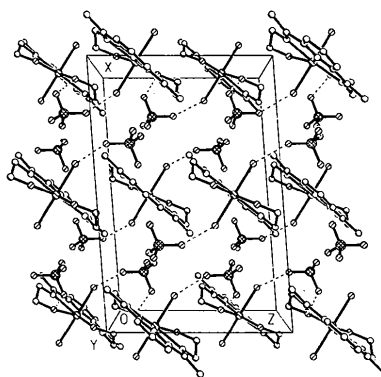

Fig. 3. Perspective view of [Mn(L)(N$_3$)$_2$], (III).

Fig. 4. Packing diagram for (I) showing the major occupancy ClO$_4^-$ site. Hydrogen bonds are shown as dashed lines.
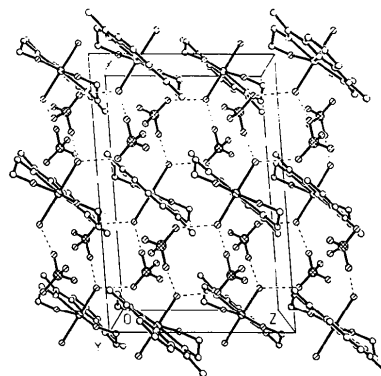
Fig. 5. Packing diagram for (I) showing the minor occupancy ClO$_4^-$ site. Hydrogen bonds are shown as dashed lines.
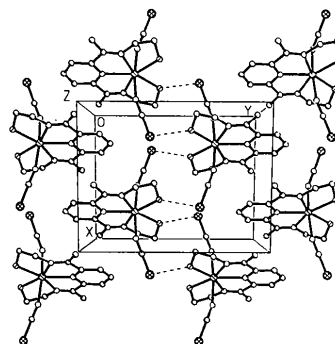

Fig. 6. Packing diagram for (II). Hydrogen bonds are shown as dashed lines.
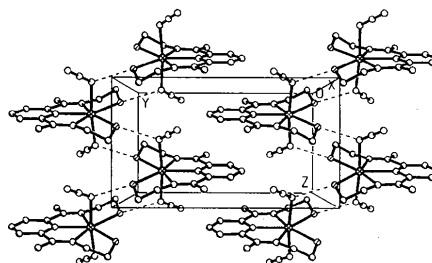

Fig. 7. Packing diagram for (III). Hydrogen bonds are shown as dashed lines.

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Structure of μ-Carbonato-1κ²*O*¹,*O*²:2κ²*O*¹,*O*³-bis[(acetylacetonato)-(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)nickel(II)] (Acetylacetonato)aqua-(methanol)(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)nickel(II) Tetraphenylborate

By KASUMI YAMADA AND KAYAKO HORI

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo 112, Japan

AND YUTAKA FUKUDA*

Coordination Chemistry Laboratory, Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Abstract. [Ni₂(C₅H₇O₂)₂(CO₃)(C₆H₁₆N₂)₂][Ni-(C₅H₇O₂)(C₆H₁₆N₂)(CH₄O)(H₂O)](C₂₄H₂₀B), M_r = 1251.32, triclinic, $P\overline{1}$, a = 16.965 (9), b = 18.847 (8), c = 12.108 (7) Å, α = 97.41 (6), β = 95.29 (6), γ = 117.83 (3)°, V = 3344 (3) Å³, Z = 2, D_x = 1.243 g cm⁻³, λ(Mo $K\alpha$) = 0.71069 Å, μ = 8.94 cm⁻¹, $F(000)$ = 1336, T = 295 K, R = 0.058, wR = 0.066 for 11 335 independent reflections. This crystal contains a μ-carbonato-bridged nickel(II) binuclear complex moiety, a mononuclear octahedral nickel(II) complex cation coordinated with a water and a methanol molecule and a tetraphenylborate moiety as counterion.

Introduction. Continuing our work on mixed-ligand complexes containing *N*-alkylated ethylenediamine [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen)] and β-diketonate ligands [acetylacetonate (acac)], we obtained bluish green lozenge-shaped crystals of the title complex from a methanol solution. Its crystal structure has been determined, by a single-crystal X-ray analysis, to be made up of [(acac)(tmen)Ni-(CO₃)Ni(tmen)(acac)] and [Ni(acac)(tmen)(H₂O)-

(CH₃OH)]BPh₄. This structure is consistent with the results of elemental analysis: H: 7.45 (7.65), C: 56.90 (56.63), H: 6.86 (6.72)%; the values in parentheses are calculated for C₅₉H₉₅BN₆Ni₃O₁₁. It is noteworthy that (*a*) it is a novel example of a binuclear complex which contains one carbonate acting as a bridging bidentate ligand and (*b*) in the same unit cell, there are two kinds of complex, binuclear and mononuclear.

Experimental. Synthesis: [Ni(acac)(tmen)]BPh₄ was dissolved in a mixture of acetonitrile and methanol, and to this solution oxamide and potassium hydroxide dissolved in water were added to form a bluish green solution. After drying, bluish green crystals were obtained, which were recrystallized from methanol. Approximate crystal dimensions 0.3 × 0.3 × 0.3 mm. Rigaku AFC-5*R* off-centered diffractometer with graphite-monochromatized Mo *K*α radiation. Cell parameters refined by least-squares method on the basis of 17 independent 2θ values, 20 < 2θ < 25°. Three-dimensional intensity data collected up to 2θ = 50°; range of *hkl*, −20 to 20, −22 to 22 and 0 to 14. 2θ–ω scan technique with scan widths of Δω = (1.0 + 0.35tanθ)°, scan speed 4° min⁻¹(2θ). Three