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Acta Cryst. (1987). C**43**, 236–238

Structure of Bis(2-methyl-1,2-propanediamine)nickel(II) Diperchlorate

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(*Received* 17 *June* 1986; *accepted* 4 *August* 1986)

Abstract. [Ni($C_4H_{12}N_2$)$_2$](ClO$_4$)$_2$, $M_r = 433{\cdot}92$, monoclinic, space group $P2_1/c$, $a = 14{\cdot}0377\,(21)$, $b = 13{\cdot}0379\,(10)$, $c = 20{\cdot}2665\,(17)$ Å, $\beta = 108{\cdot}11\,(1)°$, $V = 3525{\cdot}4\,(7)$ Å^3, $Z = 8$, $D_m = 1{\cdot}65\,(1)$, $D_x = 1{\cdot}63$ Mg m^{-3}, Cu $K\alpha$ radiation (graphite crystal monochromator, $\lambda = 1{\cdot}54184$ Å), $\mu = 4{\cdot}837$ mm^{-1}, $T = 290$ K, $F(000) = 1808$. Final $R = 0{\cdot}072$, $wR = 0{\cdot}079$ for 3724 'observed' reflections and 522 variables. The structure consists of two [Ni($C_4H_{12}N_2$)$_2$]$^{2+}$ cations and four (ClO$_4$)$^-$ anions in the asymmetric unit. The central Ni atom is square-planar coordinated, by two 2-methyl-1,2-propanediamine ligands. Distances and angles are normal [averages Ni—N(CMe$_2$) 1·905 (8) Å, Ni—N(CH$_2$) 1·916 (9) Å and N—Ni—N bite angle, 86·0 (4)°]. The perchlorate anions are disordered; also two terminal methyl groups have abnormally large temperature factors.

Introduction. As a continuation of our investigation on the structures of Ni complexes, the crystal structure of a complex with 2-methyl-1,2-propanediamine has been determined. In previous work (García-Granda & Gómez-Beltrán, 1984) we have determined the crystal structure of bis(2-methyl-1,2-propanediamine-*N,N'*)-bis(trichloroacetato-*O*)nickel(II), an octahedral complex with the same diamine as ligand. This investigation was undertaken in order to obtain enough structural data to understand the chemical and physicochemical behaviour of Ni in complexes with different C-substituted derivatives of ethylenediamine.

Experimental. A yellow crystal of approximately 0·25 × 0·20 × 0·08 mm was used for the measurements. Density measured by flotation. Throughout the experiment Cu $K\alpha$ radiation was used with a graphite crystal monochromator on a Nonius CAD-4 single-crystal diffractometer ($\lambda = 1{\cdot}54184$ Å). The unit-cell dimensions were determined from the angular settings of 25 reflections. The intensities of 13 652 reflections (one half sphere up to $\theta = 70°$), *hkl* range from (−17,−15,0) to (17,15,24) were measured, using the ω–2θ scan technique, with a scan angle of 1·50° and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 min. The final drift correction factors were between 1·00 and 1·24. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction was applied, using ψ scans (North, Phillips & Mathews, 1968), μ(Cu $K\alpha$) = 4·837 mm^{-1} (correction factors were in the range 1·00 to 0·55). Symmetry-equivalent reflections were averaged, $R_{\rm int} = \sum(I - \langle I\rangle)/\sum I = 0{\cdot}039$, resulting in 6665 unique reflections of which 3724 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values.

The structure was solved automatically, using *PATSYS* (Behm & Beurskens, 1985): the positions of the two Ni atoms were located from the Patterson map (Sheldrick, 1983), and input to *DIRDIF* (Beurskens *et al.*, 1982), and the positions of all non-hydrogen atoms were obtained. From the beginning of the refinement exceptionally high temperature factors for the O atoms

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0108-2701/87/020236-03$01.50

and C(223) and C(224) indicated that these atoms were affected by some disorder. Only for one perchlorate ion could alternative positions for the four O atoms be found and, for this model, coordinates and one common isotropic thermal factor for each group were refined. Isotropic least-squares refinement using *SHELX* (Sheldrick, 1976) converged to $R = 0{\cdot}129$. At this stage empirical absorption correction was applied (Walker & Stuart, 1983), resulting in a further decrease of R to 0·125.

Most of the H atoms were located by difference Fourier synthesis; only those bonded to C(222), C(223) and C(224) were placed in calculated positions and refined as part of rigid groups. During the final stages of the refinement the positional parameters of all atoms, except the above-mentioned H atoms, were refined; C(223), C(224) and the O atoms attached to Cl(4) were refined with isotropic temperature factors, the remaining non-hydrogen atoms with anisotropic thermal parameters. The H atoms had fixed isotropic temperature factors of 0·06 Å^2 except those attached to C(222), C(223) and C(224), which were refined with fixed temperature factors of 0·09 Å^2. The final $R = 0{\cdot}072$ and $wR = 0{\cdot}079$ for the 3724 'observed' reflections and 522 variables. The function minimized was $\sum w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0{\cdot}00090F_o^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift-to-e.s.d. ratio in the last full-matrix least-squares cycle was less than 0·61. The final difference Fourier map showed one peak of +0·75 e Å^{-3} near to the second perchlorate anion, all other residual electron density is within ±0·40 e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Figures are drawn with *PLUTO* (Motherwell, 1976). Geometrical parameters are calculated with *PARST* (Nardelli, 1983). Final positional and thermal parameters are given in Table 1.*

Discussion. Bond lengths are listed in Table 2. The structure consists of $[\mathrm{Ni(C_4H_{12}N_2)_2}]^{2+}$ cations and $(\mathrm{ClO_4})^-$ anions. There are two cations and the corresponding four anions in the asymmetric unit. Cations and anions are linked in a three-dimensional network by N—H···O hydrogen bonds. A view of the cations, and anions, showing the geometry and the crystallographic numbering scheme, is shown in Fig. 1; alternative positions for disordered oxygens [O(4*i*), *i* = 5–8] have been removed from this figure. A stereoview of the complex cation, H atoms included, is

Table 1. *Fractional positional and thermal parameters* (Å^2 × 100) (*with e.s.d.'s*)

$$U_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni(1)	0·07383 (9)	0·87105 (9)	0·25090 (6)	3·51 (4)
Cl(1)	−0·11167 (17)	0·68120 (17)	0·26488 (14)	6·32 (10)
Cl(2)	0·22743 (16)	0·54287 (19)	0·17449 (14)	6·26 (9)
O(11)	−0·0176 (5)	0·6526 (5)	0·2565 (4)	7·3 (3)
O(12)	−0·1720 (5)	0·5931 (5)	0·2614 (4)	9·1 (4)
O(13)	−0·1578 (6)	0·7521 (7)	0·2128 (6)	13·1 (5)
O(14)	−0·0949 (7)	0·7284 (7)	0·3305 (5)	13·0 (5)
O(21)	0·1862 (8)	0·4576 (9)	0·1462 (10)	22·9 (10)
O(22)	0·3220 (6)	0·5251 (9)	0·2194 (5)	13·2 (5)
O(23)	0·1579 (7)	0·5846 (7)	0·2051 (7)	16·0 (7)
O(24)	0·2369 (9)	0·6161 (11)	0·1281 (7)	19·1 (8)
N(111)	0·1233 (5)	0·8257 (6)	0·1782 (4)	4·94 (26)
N(112)	−0·0278 (6)	0·9393 (7)	0·1792 (4)	5·3 (3)
N(121)	0·0303 (6)	0·9246 (6)	0·3239 (4)	4·79 (27)
N(122)	0·1732 (5)	0·7980 (5)	0·3222 (4)	4·34 (25)
C(111)	0·0503 (6)	0·8460 (6)	0·1075 (4)	4·6 (3)
C(112)	−0·0016 (8)	0·9436 (7)	0·1142 (5)	5·9 (4)
C(113)	−0·0231 (9)	0·7573 (10)	0·0889 (7)	7·1 (5)
C(114)	0·1036 (10)	0·8564 (9)	0·0524 (6)	7·8 (5)
C(121)	0·1089 (6)	0·9134 (6)	0·3927 (4)	4·9 (3)
C(122)	0·1517 (8)	0·8076 (8)	0·3890 (5)	5·5 (4)
C(123)	0·1820 (11)	0·9966 (9)	0·4009 (7)	7·4 (5)
C(124)	0·0573 (11)	0·9176 (10)	0·4501 (6)	8·4 (5)
Ni(2)	0·42356 (9)	0·21058 (10)	0·24694 (6)	4·01 (4)
Cl(3)	0·60828 (17)	0·39629 (19)	0·22386 (16)	7·13 (11)
Cl(4)	0·70306 (24)	0·02560 (24)	0·08972 (16)	8·61 (13)
O(31)	0·5089 (5)	0·4177 (6)	0·2199 (6)	12·6 (5)
O(32)	0·6738 (7)	0·4519 (8)	0·2784 (7)	16·4 (6)
O(33)	0·6326 (6)	0·2911 (5)	0·2339 (5)	11·4 (5)
O(34)	0·6275 (9)	0·4270 (11)	0·1659 (6)	19·0 (8)
O(41)*	0·7362 (19)	−0·0796 (20)	0·0901 (11)	12·9 (3)
O(42)*	0·6535 (15)	0·1104 (16)	0·1057 (10)	12·9 (3)
O(43)*	0·7463 (16)	0·0593 (16)	0·0423 (11)	12·9 (3)
O(44)*	0·7882 (15)	0·0807 (15)	0·1313 (11)	12·9 (3)
O(45)*	0·6469 (19)	0·0450 (18)	0·0137 (12)	14·5 (4)
O(46)*	0·7469 (21)	−0·0661 (23)	0·1223 (12)	14·5 (4)
O(47)*	0·6484 (18)	−0·0162 (18)	0·0273 (13)	14·5 (4)
O(48)*	0·6198 (16)	0·0185 (18)	0·1215 (12)	14·5 (4)
N(211)	0·3322 (5)	0·2707 (6)	0·1660 (4)	4·87 (26)
N(212)	0·4691 (7)	0·1294 (7)	0·1838 (5)	5·8 (3)
N(221)	0·5163 (6)	0·1524 (7)	0·3277 (5)	6·0 (3)
N(222)	0·3764 (6)	0·2924 (6)	0·3088 (4)	6·1 (3)
C(211)	0·3296 (6)	0·2157 (7)	0·1010 (4)	5·3 (3)
C(212)	0·4341 (8)	0·1755 (10)	0·1134 (5)	6·6 (4)
C(213)	0·2513 (9)	0·1315 (9)	0·0894 (6)	7·8 (5)
C(214)	0·2998 (13)	0·2925 (13)	0·0397 (6)	9·3 (6)
C(221)	0·5102 (7)	0·2010 (8)	0·3926 (5)	6·1 (4)
C(222)	0·4078 (11)	0·2385 (14)	0·3794 (6)	10·7 (6)
C(223)	0·5852 (13)	0·2898 (13)	0·4066 (8)	15·4 (7)
C(224)	0·5511 (13)	0·1232 (12)	0·4527 (6)	14·5 (6)

* Occupation factor 0·5.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

Ni(1)—N(111)	1·908 (8)	Ni(2)—N(221)	1·904 (8)
Ni(1)—N(112)	1·910 (8)	Ni(2)—N(222)	1·915 (8)
Ni(1)—N(121)	1·900 (9)	Cl(3)—O(31)	1·400 (8)
Ni(1)—N(122)	1·920 (6)	Cl(3)—O(32)	1·401 (11)
Cl(1)—O(11)	1·432 (8)	Cl(3)—O(33)	1·413 (8)
Cl(1)—O(12)	1·416 (8)	Cl(3)—O(34)	1·346 (15)
Cl(1)—O(13)	1·401 (10)	Cl(4)—O(41)	1·447 (26)
Cl(1)—O(14)	1·418 (11)	Cl(4)—O(42)	1·397 (22)
Cl(2)—O(21)	1·302 (12)	Cl(4)—O(43)	1·358 (25)
Cl(2)—O(22)	1·376 (8)	Cl(4)—O(44)	1·423 (19)
Cl(2)—O(23)	1·418 (13)	Cl(4)—O(45)	1·518 (23)
Cl(2)—O(24)	1·376 (15)	Cl(4)—O(46)	1·411 (28)
N(111)—C(111)	1·504 (9)	Cl(4)—O(47)	1·372 (24)
N(112)—C(112)	1·476 (15)	Cl(4)—O(48)	1·502 (26)
N(121)—C(121)	1·492 (10)	N(211)—C(211)	1·489 (12)
N(122)—C(122)	1·482 (14)	N(212)—C(212)	1·483 (14)
C(111)—C(112)	1·494 (13)	N(221)—C(221)	1·487 (14)
C(111)—C(113)	1·516 (15)	N(222)—C(222)	1·531 (15)
C(111)—C(114)	1·532 (17)	C(211)—C(212)	1·504 (14)
C(121)—C(122)	1·516 (13)	C(211)—C(213)	1·519 (15)
C(121)—C(123)	1·467 (16)	C(211)—C(214)	1·548 (16)
C(121)—C(124)	1·551 (18)	C(221)—C(222)	1·462 (18)
Ni(2)—N(211)	1·909 (7)	C(221)—C(223)	1·531 (20)
Ni(2)—N(212)	1·917 (11)	C(221)—C(224)	1·551 (17)

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond angles, bond lengths and angles involving H atoms, selected torsion angles and angles between least-squares planes, Table 3 and Fig. 2 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43309 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

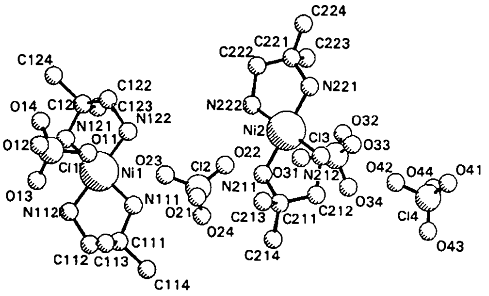

Fig. 1. View, with atom labels, of the two independent complex cations, showing the nickel coordination, and of the four perchlorate anions.

shown in Fig. 2 (deposited). The central Ni atom is square-planar coordinated by two 2-methyl-1,2-propanediamine ligands. An analysis of torsion angles shows that the arrangement of the diamine ligands around the central nickel is nearly centrosymmetric; the average value of the torsion angle N—C—C—N is 46·0 (1)° which is in good agreement with the value of 47·8 (6)° found by García-Granda & Gómez-Beltrán (1984) in the centrosymmetric octahedral trichloroacetato complex. The average Ni—N(1) and Ni—N(2) distances are respectively 1·905 (8) and 1·916 (9) Å and the average N(1)—Ni—N(2) bite angle is 86·0 (4)° compared with 2·080 (4) and 2·063 (5) Å and 82·5 (2)° in the above-mentioned octahedral complex.

Values of Ni—N distances and N—Ni—N angles for a number of nickel complexes of C-substituted ethylenediamines with square-planar coordination are collected in Table 3 (deposited). No unusual geometric features are present in the molecule.

SG-G gratefully thanks the Spanish Ministerio de Educacion y Ciencia (MEC) for a postdoctoral grant and the University of Oviedo for leave of absence.

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Acta Cryst. (1987). C**43**, 238–241

Structure du Cyclobutanedicarboxylate-1,1 Acide de Potassium

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(*Reçu le* 15 *juillet* 1985; *accepté le* 12 *septembre* 1986)

Abstract. $C_6H_7O_4^-.K^+$, $M_r = 182{\cdot}23$, orthorhombic, *Pbca*, $a = 24{\cdot}682\ (6)$, $b = 9{\cdot}132\ (2)$, $c = 6{\cdot}421\ (9)$ Å, $V = 1447{\cdot}3\ (3)$ Å^3, $Z = 8$, $D_m = 1{\cdot}66\ (1)$, $D_x = 1{\cdot}67$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 6{\cdot}7$ cm^{-1}, $F(000) = 752$, $T = 293$ K, final $R = 0{\cdot}055$ for 820 independent reflections. K^+ is surrounded by seven O atoms from four different molecules. The four C atoms in the ring have a typical sp^3 configuration and the ring has a pleated conformation. The $C_6H_7O_4^-$ anions are linked into infinite chains by short hydrogen bonds [O—H···O = 2·523 (5) Å].

Introduction. A l'exception de l'acide cyclobutanedicarboxylique-1,3-*trans* (Margulis & Fisher, 1967), les

0108-2701/87/020238-04$01.50