considerations, the fit was limited to 62 data with even I_{hex}.) It was found neccessary to include also in the least-squares fit some amount of untransformed cubic material. The resulting percentages of the five contributors together with their e.s.d.'s were:

	Twin (1)	Twin (2)	Twin (3)	Twin (4)	Untransformed
	23·9	18·3	19·1	10·5	28·1
E.s.d.	1·3	1·4	1·3	3·3	3·5

Of the four variants, only twin (4) differs significantly in amount from the average of the others; the reason for the deviation is not apparent. If in the least-squares fit the amounts for all the twin variants are constrained to be equal the fit is significantly less good (at the 99% confidence level according to the F test), and the amount of untransformed cubic material is indicated to be 17·5% with an e.s.d. of 1·4%. For the untransformed material the temperature factor B (on F) is apparently 1·53 $Å^2$, about twice the value found for the single twin variant, indicating atomic positional displacements presumably resulting from occupational disorder in the untransformed cubic phase.

Note added in proof: We have found that on annealing at 923 K ω'' transforms into the $B8_2$ or Ni_2In structure: the z parameter of Al becomes $\frac{1}{4}$ and that of Ti(2) becomes $\frac{3}{4}$, and the occupancies of 1(*a*)

and 1(*b*) become identical mixtures of Ti, Nb, and Al. The intensities of the twin reflections can be accounted for by (unequal) contributions of the four twins without any untransformed cubic material being left over.

References

AUSTIN, A. E. & DOIG, J. R. (1957). *J. Met.* **9**, 27–30.
BAGARIATSKII, YU. A. & NOSOVA, G. I. (1958). *Kristallografiya*, **3**, 17–28; *Sov. Phys. Crystallogr.* **3**, 15–26.
BENDERSKY, L. A. & BOETTINGER, W. J. (1988). *Conf. Proc. Mater. Res. Soc.* Boston, USA.
GEORGOPOLOUS, P. & COHEN, D. B. (1981). *Acta Metall.* **29**, 1535–1551.
International Tables for X-ray Crystallography (1974). Vol. IV, pp 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Molecular Structure Corporation (1985). *TEXRAY*. 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
PRASETYO, A., REYNAUD, A. & WARLIMONT, H. (1976). *Acta Metall.* **24**, 1009–1016.
SILCOCK, J. M. (1958). *Acta Metall.* **6**, 481–493.
WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

Structure of Bis(acetato)bis(*meso*-1,2-diphenyl-1,2-ethanediamine)nickel(II) Trihydrate, [Ni($C_2H_3O_2$)$_2$($C_{14}H_{16}N_2$)$_2$].3H_2O

BY S. GARCÍA-GRANDA, M. R. DÍAZ, C. BARRIO AND F. GÓMEZ-BELTRÁN

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, Julian Clavería S/N 33006, Oviedo, Spain

Abstract. [Ni($C_2H_3O_2$)$_2$($C_{14}H_{16}N_2$)$_2$].3H_2O, $M_r = 655\cdot43$, monoclinic, $C2/c$, $a = 30\cdot7007$ (3), $b = 7\cdot1898$ (4), $c = 22\cdot7114$ (7) Å, $\beta = 138\cdot513$ (2)°, $V = 3321\cdot0$ (3) Å^3, $Z = 4$, $D_x = 1\cdot28$ Mg m^{-3}. Mo $K\alpha$ radiation (graphite crystal monochromator, $\lambda = 0\cdot71073$ Å), μ(Mo $K\alpha$) $= 0\cdot630$ mm^{-1}, $F(000) = 1392$, $T = 293$ K. Final conventional R factor $= 0\cdot035$ for 4842 unique reflections. Distances Ni—N(1) and Ni—N(2) are 2·082 (4) and 2·127 (4) Å respectively and the N(1)—Ni—N(2) bite angle is 79·8 (1)°. The nickel coordination is pseudo-octahedral, with two diamine ligands on a plane and two acetates in *trans* position.

Introduction. The crystal and molecular structure of the title compound was determined as part of our work on nickel complexes and C-substituted 1,2-ethanediamines. In a previous communication we reported a square-planar complex of nickel(II) with *meso*-stien (García-Granda & Gómez-Beltrán, 1984*b*). As far as we know no crystal structure of a blue complex of nickel(II) and *meso*-1,2-diphenyl-1,2-ethanediamine (*meso*-stien), has been reported, with the exception of a paper by Nyburg & Wood (1964) where a crystal structure containing yellow and blue forms of bis(*meso*-stien)nickel(II) bis(dichloroacetate) was described. The present paper

Table 1. Fractional positional and thermal parameters (Å² × 10²), e.s.d.'s in parentheses

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni(1)	0·25000 (0)	0·7500 (0)	0·00000 (0)	3·32 (6)
O(1)	0·19705 (22)	0·1946 (5)	0·0137 (3)	6·8 (4)
O(2)	0·50000 (0)	0·1475 (11)	0·75000 (0)	10·3 (8)
O(3)	0·17691 (14)	0·8016 (3)	−0·00861 (17)	3·93 (24)
O(4)	0·12451 (16)	0·5309 (4)	−0·05913 (24)	6·7 (4)
N(1)	0·28718 (18)	0·5261 (5)	0·08500 (24)	3·7 (3)
N(2)	0·32197 (20)	0·8882 (5)	0·12427 (26)	3·7 (3)
C(1)	0·35686 (21)	0·5636 (5)	0·16731 (26)	3·4 (3)
C(11)	0·39263 (19)	0·4131 (5)	0·23796 (26)	3·8 (3)
C(12)	0·36351 (24)	0·3183 (6)	0·2544 (3)	4·5 (4)
C(13)	0·3991 (3)	0·1912 (6)	0·3240 (3)	5·4 (5)
C(14)	0·4627 (3)	0·1551 (7)	0·3753 (4)	6·6 (5)
C(15)	0·49277 (27)	0·2431 (9)	0·3597 (3)	7·1 (4)
C(16)	0·45768 (24)	0·3743 (7)	0·2907 (3)	5·5 (4)
C(2)	0·36265 (20)	0·7593 (7)	0·20171 (25)	3·6 (3)
C(21)	0·34451 (19)	0·7626 (6)	0·24830 (24)	3·7 (3)
C(22)	0·28208 (24)	0·8105 (6)	0·2049 (3)	4·6 (4)
C(23)	0·2683 (3)	0·8158 (7)	0·2510 (4)	6·0 (5)
C(24)	0·3158 (3)	0·7701 (8)	0·3399 (4)	6·6 (5)
C(25)	0·3772 (3)	0·7214 (7)	0·3827 (4)	5·9 (5)
C(26)	0·39205 (26)	0·7161 (6)	0·3380 (3)	4·7 (4)
C(3)	0·13549 (23)	0·6900 (6)	−0·0282 (3)	4·3 (4)
C(4)	0·09569 (26)	0·7553 (9)	−0·0167 (4)	7·4 (5)

Table 2. Bond lengths (Å) and bond angles (°), with e.s.d.'s in parentheses

Ni(1)—N(1)	2·082 (4)		C(15)—C(16)	1·410 (7)
Ni(1)—N(2)	2·127 (4)		C(2)—C(21)	1·522 (5)
Ni(1)—O(3)	2·133 (3)		C(21)—C(22)	1·391 (6)
N(1)—C(1)	1·472 (5)		C(21)—C(26)	1·398 (6)
N(2)—C(2)	1·494 (5)		C(22)—C(23)	1·393 (6)
C(1)—C(11)	1·524 (5)		C(23)—C(24)	1·384 (7)
C(1)—C(2)	1·555 (5)		C(24)—C(25)	1·370 (7)
C(11)—C(12)	1·379 (6)		C(25)—C(26)	1·393 (6)
C(11)—C(16)	1·386 (6)		O(3)—C(3)	1·269 (5)
C(12)—C(13)	1·397 (6)		O(4)—C(3)	1·250 (5)
C(13)—C(14)	1·354 (7)		C(3)—C(4)	1·502 (6)
C(14)—C(15)	1·364 (7)			

N(1)—Ni(1)—N(2)	79·8 (1)		N(2)—C(2)—C(1)	106·7 (3)
N(1)—Ni(1)—O(3)	91·6 (1)		N(2)—C(2)—C(21)	113·2 (4)
N(2)—Ni(1)—O(3)	91·0 (1)		C(1)—C(2)—C(21)	113·6 (4)
Ni(1)—N(1)—C(1)	107·9 (3)		C(2)—C(21)—C(22)	122·4 (4)
Ni(1)—N(2)—C(2)	113·6 (3)		C(2)—C(21)—C(26)	119·1 (4)
N(1)—C(1)—C(11)	115·4 (3)		C(22)—C(21)—C(26)	118·5 (4)
N(1)—C(1)—C(2)	108·5 (3)		C(21)—C(22)—C(23)	120·2 (4)
C(11)—C(1)—C(2)	113·0 (3)		C(22)—C(23)—C(24)	120·9 (5)
C(1)—C(11)—C(12)	122·3 (4)		C(23)—C(24)—C(25)	119·1 (5)
C(1)—C(11)—C(16)	119·5 (4)		C(24)—C(25)—C(26)	120·9 (5)
C(12)—C(11)—C(16)	118·1 (4)		C(21)—C(26)—C(25)	120·3 (5)
C(11)—C(12)—C(13)	120·9 (5)		Ni(1)—O(3)—C(3)	129·1 (3)
C(12)—C(13)—C(14)	120·3 (5)		O(3)—C(3)—O(4)	123·7 (4)
C(13)—C(14)—C(15)	120·4 (5)		O(3)—C(3)—C(4)	118·1 (4)
C(14)—C(15)—C(16)	119·8 (5)		O(4)—C(3)—C(4)	118·1 (4)
C(11)—C(16)—C(15)	120·4 (5)			

reports the crystal and molecular structure of a new pseudo-octahedral complex of nickel(II).

Experimental. Blue crystal, 0·2 × 0·07 × 0·1 mm. Mo $K\alpha$ radiation, graphite crystal monochromator, Nonius CAD-4 single-crystal diffractometer ($\lambda = 0\cdot71073$ Å). Unit-cell dimensions were determined from the angular settings of 25 reflections with $20 < \theta < 30°$. Space group $C2/c$ from systematic absences

and structure determination. 11433 reflections were measured, hkl range $-42, -10, -11$ to 28,10,31, $0 < \theta < 30°$; $\omega-2\theta$ scan technique with a variable scan rate and a maximum scan time of 60 s per reflection. Intensity was checked throughout data collection by monitoring three standard reflections every 60 min. Final drift corrections were between 0·97 and 1·01. On all reflections, profile analysis performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction applied, using ψ scans (North, Phillips & Mathews, 1968), μ(Mo $K\alpha$) $= 6\cdot30$ cm^{-1} (correction factors range from 0·31 to 1·00). Symmetry equivalent reflections were averaged, $R_{int} = \Sigma(I - \langle I\rangle)/\Sigma I = 0\cdot070$, 4842 unique reflections and 1463 observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and data reduced to $|F_o|$ values. Structure was solved by direct methods using the program SHELX86 (Sheldrick, 1985) and Fourier synthesis. Isotropic least-squares refinement, using SHELX (Sheldrick, 1976), converged to $R = 0\cdot128$. Additional empirical absorption correction was applied (Walker & Stuart, 1983). Maximum and minimum correction factors 1·67 and 0·63. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of all the hydrogen atoms.

Positional parameters and anisotropic thermal parameters of the non-hydrogen atoms were refined. All hydrogen atoms were refined isotropically except those of the methyl group belonging to the acetate, which were refined riding on the parent atom, C(4). The final conventional agreement factors were $R = 0\cdot035$ and $wR = 0\cdot034$ for the 1463 'observed' reflections and 282 variables. Function minimized $\Sigma w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0\cdot00040F_o{}^2]$ with $\sigma(F_o)$ from counting statistics. Maximum shift to e.s.d. ratio in the last full-matrix least-squares cycle was less than 0·18. Final difference Fourier map showed no peaks higher than 0·25 e Å^{-3} or deeper than $-0\cdot29$ e Å^{-3}. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). The plot was made with the PLUTO program (Motherwell, 1976). Geometrical calculations were made with PARST (Nardelli, 1983).
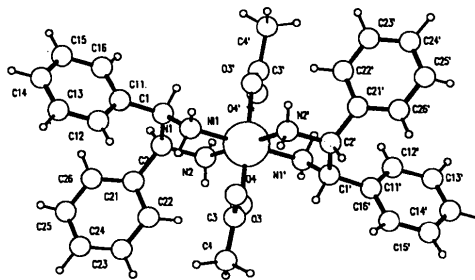

Fig. 1. PLUTO (Motherwell, 1976) plot showing the coordination of the central nickel and the atomic numbering.

Discussion. Final positional and thermal parameters are given in Table 1.* Molecular geometry data are collected in Table 2. Fig. 1 shows the nickel coordination and the atomic numbering scheme. The complex molecules are centrosymmetrical. The nickel atoms lie on symmetry centers, and the oxygen, O(2), of a water molecule, on a mirror plane. The central nickel is pseudo-octahedrally coordinated by two meso-stien ligands and two acetates. The Ni—N distances (Table 2) are the usual distances found in pseudo-octahedral coordination, similar to 2·080 (4), 2·063 (5) and 2·103 (4) Å, found for bis(2-methyl-1,2-propanediamine)bis(trichloroacetato)nickel(II) (García-Granda & Gómez-Beltrán, 1984a). The N(1)—Ni—N(2) bite angle, 79·8 (1)°, and the N(1)—Ni—O(3) and N(2)—Ni—O(3) angles of 91·6 (1) and 91·0 (1)° are very close to the respective values of 82·5 (2), 91·1 (2) and 84·7 (2)° found in the cited compound. The angle between the plane through N(1)—Ni—N(2), and Ni(1)—O(3), is 88·3 (2)°. The octahedral coordination of this complex confirms the lack of steric hindrance expected from the structure of bis(meso-1,2-diphenyl-1,2-ethanediamine)nickel(II) dichloride dihydrate

---

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, hydrogen-bond distances and angles, least-squares-planes data and principal torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52332 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(García-Granda & Gómez-Beltrán, 1984b). Both molecules show a similar disposition of the meso-stien ligands, the torsion angle C(11)—C(1)—C(2)—C(21) being 51·1 (6)° in the present compound and 55·6 (6)° in the square-planar complex. The Ni—N distances are sensibly longer in an octahedral coordination than in the square-planar complex [1·922 (4) Å]. Water molecules contribute to the molecular packing through hydrogen bridges. There is also one intramolecular hydrogen bond connecting N(2) with the free oxygen of the acetate group O(4).

References

García-Granda, S. & Gómez-Beltrán, F. (1984a). Acta Cryst. C40, 949–951.
García-Granda, S. & Gómez-Beltrán, F. (1984b). Acta Cryst. C40, 2037–2038.
Grant, D. F. & Gabe, E. J. (1978). J. Appl. Cryst. 11, 114–120.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Lehmann, M. S. & Larsen, F. K. (1974). Acta Cryst. A30, 580–584.
Motherwell, W. D. S. (1976). PLUTO. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Nardelli, M. (1983). Comput. Chem. 7, 95–98.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). Acta Cryst. A24, 351–359.
Nyburg, S. C. & Wood, J. S. (1964). Inorg. Chem. 3, 468–476.
Sheldrick, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1985). SHELX86. In Crystallographic Computing 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford: Clarendon Press.
Walker, N. & Stuart, D. (1983). Acta Cryst. A39, 158–166.

Structure and Single-Crystal Conductivity Measurements of Oxidized 3d Metal Phthalocyanines. Bis-Chloro Derivatives of Chromium(III), Iron(III) and Cobalt(III)

By Boujemaa Moubaraki, Magali Ley and David Benlian*

Laboratoire de Chimie de Coordination, CNRS-CRL400035, Université de Provence–Faculté St Jérôme-D22, Avenue de l'Escadrille Normandie-Niemen, F13397 Marseille CEDEX 13, France

and Jean-Pierre Sorbier

Laboratoire d'Electronique des Milieux Condensés, CNRS-UA784, Université de Provence–Faculté St Jérôme-D22, Avenue de l'Escadrille Normandie-Niemen, F13397 Marseille CEDEX 13, France

Abstract. Dichloro(phthalocyaninato)iron(III), [Fe(C$_{32}$H$_{16}$N$_8$)Cl$_2$], M_r = 639·7, monoclinic, $P2_1/n$, a = 9·023 (2), b = 14·588 (2), c = 10·216 (5) Å, β = 97·58 (1)°, V = 1333·2 (7) Å^3, Z = 2, D_m = 1·57, D_x = 1·592 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·805 mm^{-1}, $F(000)$ = 648, T = 298 K, R = 0·036, wR = 0·044 for 1510 reflections. Dichloro(phthalocyaninato)chromium(III), [Cr(C$_{32}$H$_{16}$N$_8$)Cl$_2$], M_r =

---

* To whom correspondence should be addressed.