$\frac{1}{2}-z$). The resulting four-membered ring is significantly puckered as can be seen from the dihedral angles between the $\mathrm{CdO(1)O(1^i)}$ and $\mathrm{Cd^iO(1)O(1^i)}$ planes, 156·1 (4)°, and between the $\mathrm{CdCd^iO(1)}$ and $\mathrm{CdCd^iO(1^i)}$ planes, 150·0 (3)°.

The coordination polyhedron around Cd can be approximated as a strongly distorted octahedron formed by the saden ligand atoms N(1), N(2), N(3), O(1) and $\mathrm{O(1^i)}$, and by the O(6) atom of ethanol. The Cd, N(2), N(3), O(1), $\mathrm{O(1^i)}$ atoms are coplanar within $\pm$0·077 (8) Å. Fig. 2 shows a perspective view of the coordination environment of the Cd atom. Since the saden ligand is designed perfectly to accommodate small metal ions into a square planar cage formed by its four donor atoms, it is not surprising that the large Cd^{2+} ion (which moreover displays a profound tendency to higher coordination numbers than four) has a considerably distorted environment in its saden complex. In contrast, distortions within the ligand backbone are relatively small. When compared to, *e.g.*, the Ni (Podlahová, Knížek, Loub & Hašek, 1988) and Pd (Kratochvíl, Nováková, Haber, Ondráček & Hájek, 1989) complexes, the most important difference concerns the N(2)—*M* ring junction which is *trans* for M = Ni, Pd but *cis* for M = Cd, in agreement with folding of the ligand in order to enable a facial coordination of its N atoms. Further, both five-membered chelate rings of the Cd complex assume a half-chair conformation in contrast to the Ni and Pd complexes where the rings involving N(2) and N(3) are envelopes. Finally, all three chelate rings in the Cd complex are significantly more puckered than their Ni and Pd analogues. This can be demonstrated by the N(1)—C(1)—C(2)—N(2), N(2)—C(3)—C(4)—N(3) and *M*—N(3)—C(5)—C(6) torsion angles whose absolute values are 63·0 (5), 54·4 (5) and 6·8 (6)° for Cd, 50·6 (7), 42·1 (6) and 2·3 (5)° for Ni, and 53·2 (7), 46·1 (6) and 3·2 (6)° for Pd. The conformation of the six-membered chelate ring is close to a very flat distorted boat.

The bonding between the complex cations and the perchlorate anions is predominantly ionic, the shortest distance being 3·08 (1) Å between O(2) and $\mathrm{N(2^i)}$ with the geometry at $\mathrm{H(N2^i)}$ satisfying the criterion for a weak hydrogen bond (Taylor & Kennard, 1982): $\mathrm{O(2)\cdots H(N2^i)}$ 2·37 Å, $\mathrm{O(2)\cdots H(N2^i)—N(2^i)}$ 121°.

References

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Jones, R. D., Summerville, D. A. & Basolo, F. (1979). *Chem. Rev.* **79**(2), 139–179.

Kratochvíl, B., Nováková, M., Haber, V., Ondráček, J. & Hájek, B. (1989). *Acta Cryst.* C**45**, 403–405.

Loub, J., Podlahová, J., Kopf, J. & Weiss, E. (1989). *Acta Cryst.* C**45**, 406–407.

Podlahová, J., Knížek, K., Loub, J. & Hašek, J. (1988). *Acta Cryst.* C**44**, 631–633.

Rotondo, E., Cusmano Priolo, F. C., Romeo, M., Bruno, G. & Bombieri, G. (1983). *Acta Cryst.* C**39**, 1525–1527.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS*86. Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.

Acta Cryst. (1990). C**46**, 598–600

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

By S. García-Granda, M. R. Díaz and F. Gómez-Beltrán

Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo,
Julián Clavería s/n 33006, *Oviedo, Spain*

(*Received* 25 *May* 1989; *accepted* 14 *August* 1989)

Abstract. $[Ni(C_4H_{12}N_2)_2]Br_2$, M_r = 394·81, triclinic, $P\bar{1}$, a = 13·4387 (1), b = 9·6298 (1), c = 5·9928 (1) Å, α = 85·391 (1), β = 84·714 (1), γ = 72·558 (1)°, V = 735·60 (2) Å^3, Z = 2, D_x = 1·78 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 6·687 mm^{-1}, F(000) = 396, T = 293 K. Final R = 0·034 for 2054 observed reflections and 232 variables. Ni—N(1) and Ni—N(2) average distances are 1·907 (5) and 1·919 (5) Å, respectively, and the average N(1)—Ni—N(2) bite angle is 86·2 (2)°. The nickel coordination is pseudo square-planar, with two diamine ligands close to a plane. The ligands show an unusual non-centrosymmetric disposition around the central nickel, being related by a pseudo-mirror plane.

Introduction. The present paper reports the crystal and molecular structure of a new complex of nickel(II). The structure of the title compound was

0108-2701/90/040598-03$03.00

determined as part of our work on nickel complexes and *C*-substituted 1,2-ethanediamines. In previous communications we reported the structures of an octahedral as well as a square-planar complex with nickel(II) and 2-methyl-1,2-propanediamine (ibn) (García-Granda & Gómez-Beltrán, 1984; García-Granda, Beurskens, Behm & Gómez-Beltrán, 1987). The crystal structure determination of both complexes showed that the Ni—N distances were slightly different depending on the substitution on the C atom attached to each nitrogen. Since the accuracy in structural parameters for the square-planar complex was not very high, $R = 0·072$, we undertook the structure determination of a new square-planar complex with ibn, in order to obtain more data regarding this behaviour.

Experimental. Yellow crystal, 0·23 × 0·13 × 0·03 mm. Graphite crystal monochromator, Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions determined from the angular settings of 25 reflections with $20 < \theta < 30°$. Space group $P\overline{1}$ from structure determination. 8013 reflections measured, *hkl* range $(-18, -13, -8)$ to $(18, 13, 6)$, θ limits $(0 < \theta < 30°)$. ω–2θ scan technique with a variable scan speed and a maximum scan time of 60 s per reflection. Intensity checked by monitoring three standard reflections every 60 min. Final drift corrections between 0·97 and 1·01. Profile analysis performed on all reflections (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction applied, using ψ scans (North, Phillips & Mathews, 1968), correction factors range 0·93 to 1·00. Symmetry equivalent reflections averaged, $R_{\rm int} = \sum(I - \langle I \rangle)/\sum I = 0·040$, 4303 unique reflections and 2054 observed with $I > 3\sigma(I)$. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values. Structure solved by Patterson method using the program *SHELXS*86 (Sheldrick, 1985) and Fourier synthesis. Isotropic least-squares refinement, using *SHELX* (Sheldrick, 1976), converged to $R = 0·086$. Additional empirical absorption correction applied (Walker & Stuart, 1983). Maximum and minimum correction factors 1·42 and 0·77. Further anisotropic refinements followed by a difference Fourier synthesis for location of all the H atoms. Positional parameters and anisotropic thermal parameters of the non-H atoms refined. All H atoms refined isotropically. The final conventional agreement factors were $R = 0·034$ and $wR = 0·033$ for the 2054 observed reflections and 232 variables. Function minimized $\sum w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0·00020F_o^2]$ with $\sigma(F_o)$ from counting statistics. Maximum shift over e.s.d ratio in the last full-matrix least-squares cycle less than 0·06. Final difference Fourier map showed no peaks higher than 0·66 e Å^{-3} nor deeper than $-0·55$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray*

Table 1. *Fractional positional and thermal parameters* ($\times 10^2$) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Br(1)	0·01979 (4)	0·29928 (7)	0·17732 (9)	3·64 (1)
Br(2)	0·56001 (4)	0·31411 (7)	0·19790 (9)	3·85 (1)
Ni(1)	0·23035 (5)	0·57373 (7)	0·4235 (1)	2·42 (1)
N(11)	0·3480 (3)	0·4410 (5)	0·5590 (8)	2·6 (2)
N(12)	0·1571 (4)	0·4344 (5)	0·5195 (8)	3·0 (2)
N(21)	0·3008 (4)	0·7167 (5)	0·3419 (8)	2·6 (2)
N(22)	0·1115 (4)	0·7098 (6)	0·2923 (8)	3·4 (2)
C(11)	0·3170 (4)	0·3266 (6)	0·710 (9)	3·0 (2)
C(12)	0·2316 (5)	0·2934 (7)	0·595 (1)	3·6 (2)
C(13)	0·4097 (6)	0·1915 (8)	0·740 (1)	4·7 (3)
C(14)	0·2757 (5)	0·3935 (8)	0·935 (1)	4·1 (3)
C(21)	0·2229 (4)	0·8647 (6)	0·3122 (8)	2·9 (2)
C(22)	0·1400 (5)	0·8370 (7)	0·180 (1)	3·7 (2)
C(23)	0·2746 (6)	0·9699 (7)	0·186 (1)	4·2 (3)
C(24)	0·1790 (5)	0·9192 (7)	0·541 (1)	3·6 (2)

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

Ni(1)—N(11)	1·911 (5)	N(22)—C(22)	1·483 (8)
Ni(1)—N(12)	1·914 (4)	C(11)—C(12)	1·517 (8)
Ni(1)—N(21)	1·903 (4)	C(11)—C(13)	1·519 (8)
Ni(1)—N(22)	1·923 (5)	C(11)—C(14)	1·524 (8)
N(11)—C(11)	1·501 (7)	C(21)—C(22)	1·521 (8)
N(12)—C(12)	1·490 (8)	C(21)—C(23)	1·511 (8)
N(21)—C(21)	1·502 (7)	C(21)—C(24)	1·510 (7)

N(11)—Ni(1)—N(12)	86·4 (2)	C(12)—C(11)—C(13)	111·3 (5)
N(11)—Ni(1)—N(21)	93·6 (2)	N(11)—C(11)—C(14)	107·2 (5)
N(12)—Ni(1)—N(21)	177·1 (2)	C(12)—C(11)—C(14)	111·4 (5)
N(11)—Ni(1)—N(22)	178·8 (2)	C(13)—C(11)—C(14)	110·8 (5)
N(12)—Ni(1)—N(22)	93·9 (2)	N(12)—C(12)—C(11)	108·2 (4)
N(21)—Ni(1)—N(22)	86·0 (2)	N(21)—C(21)—C(22)	103·7 (4)
Ni(1)—N(11)—C(11)	111·7 (3)	N(21)—C(21)—C(23)	110·4 (4)
Ni(1)—N(12)—C(12)	110·4 (3)	C(22)—C(21)—C(23)	112·0 (5)
Ni(1)—N(21)—C(21)	110·2 (3)	N(21)—C(21)—C(24)	108·8 (4)
Ni(1)—N(22)—C(22)	110·7 (3)	C(22)—C(21)—C(24)	111·8 (5)
N(11)—C(11)—C(12)	105·1 (5)	C(23)—C(21)—C(24)	109·9 (5)
N(11)—C(11)—C(13)	110·9 (5)	N(22)—C(22)—C(21)	107·7 (4)

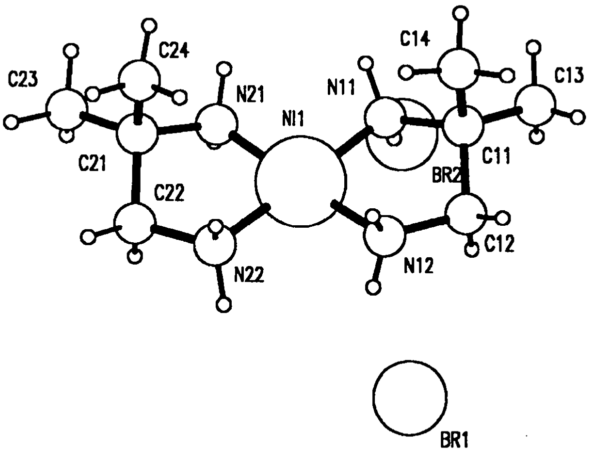

Fig. 1. *PLUTO* (Motherwell, 1976) drawing showing the coordination of central nickel and the atomic numbering scheme.

Crystallography (1974). The plot was made with *PLUTO* (Motherwell, 1976). Geometrical calculations were made with *PARST* (Nardelli, 1983). All calculations were made on a IBM 4341 computer.

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 central nickel is pseudo square-planar coordinated by two ibn ligands. The Ni—N average distances, Ni—N(1) 1·907 (5) and Ni—N(2) 1·919 (5) Å, are the usual distances in square-planar coordination, similar to the 1·904 (9) and 1·915 (7) Å found for bis(2-methyl-1,2-propanediamine)nickel(II) diperchlorate (García-Granda *et al.*, 1987). This small difference in Ni—N distances, which is systematically found in both octahedral and square-planar complexes with ibn, appears as a clear effect of the *C*-substitution. The average N(1)—Ni—N(2) bite angle, 86·2 (2)°, is similar to 86·0 (4)° found in the above-mentioned complex. The ligands show an unusual, non-centrosymmetric disposition around the central nickel, being related by a pseudo-mirror plane, which has not been observed before for this ligand. An analysis of torsion angles shows that the distortion of the diamine ligand is similar to that found in the centrosymmetric complexes of this diamine. The average value of the torsion angle N—C—C—N is 47·0 (6)°, which is in good agreement with the values of 48·7 (6) and 46·0 (1)° found by García-Granda & Gómez-Beltrán (1984) in the centrosymmetric octahedral trichloroacetate complex and by García-Granda *et al.* (1987) in the square-planar perchlorate complex respectively.

---

* 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 52491 (25 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

García-Granda, S., Beurskens, P. T., Behm, H. J. J. & Gómez-Beltrán, F. (1987). *Acta Cryst.* **C43**, 236–238.

García-Granda, S. & Gómez-Beltrán, F. (1984). *Acta Cryst.* **C40**, 949–951.

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.

Sheldrick, G. M. (1976). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86*, *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Acta Cryst. (1990). **C46**, 600–604

Molecular Structures of Caracemide,* an Inhibitor of Ribonucleotide Reductase, and of one of its Degradation Products

By Ingrid Kjøller Larsen

Department of Organic Chemistry, Royal Danish School of Pharmacy, DK-2100 Copenhagen, Denmark

(*Received* 12 *May* 1989; *accepted* 11 *July* 1989)

Abstract. *N*-Acetyl-*N*,*O*-di(methylcarbamoyl)hydroxylamine, $C_6H_{11}N_3O_4$ (CAR), $M_r = 189·18$, monoclinic, $P2_1/c$, $a = 5·012$ (1), $b = 11·989$ (2), $c = 14·375$ (2) Å, $\beta = 93·10$ (2)°, $V = 862·5$ (2) Å^3 at 105 K, $Z = 4$, $D_x = 1·457$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·115$ mm^{-1}, $F(000) = 400$, $T = 105$ K. Final $R = 0·034$ for 1351 unique observed reflections. *N*-Acetyl-*O*-methylcarbamoylhydroxylamine, $C_4H_8N_2O_3$ (DECAR), $M_r = 132·12$, orthorhombic, *Pbca*, $a = 8·975$ (2), $b = 9·748$ (1), $c = 14·2243$ (8) Å, $V = 1244·4$ (5) Å^3 at 105 K, $Z = 8$, $D_x = 1·410$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·113$ mm^{-1}, $F(000) = 560$, $T = 105$ K. Final $R = 0·034$ for 1837 unique observed reflections. Both molecules consist of two roughly planar parts with dihedral angles of 84·19 (4) and 74·87 (3)° between the planes, for CAR and DECAR, respectively. One

---

* *Chemical Abstracts* name: *N*-[(methylamino)carbonyl]-*N*-{[(methylamino)carbonyl]oxy}acetamide.

0108-2701/90/040600-05$03.00