

a fixed U_{iso} of 0.08 \AA^2) and refined on F by the full-matrix least-squares method to $R = 0.0531$, $wR = 0.0421$, $w = 1/\sigma^2(F)$, $S = 1.03$; $(\Delta/\sigma)_{max} = 0.000$; $(\Delta\rho)_{max} = 0.94$, $(\Delta\rho)_{min} = -0.56 \text{ e \AA}^{-3}$. All calculations were performed on a VAX 3200 using the *SHELXTL-Plus88* package (Sheldrick, 1988); atomic scattering factors from *SHELXTL-Plus88*.

Discussion. Final atomic coordinates and equivalent isotropic atomic displacement factors are listed in Table 1.* The structure contains the centrosymmetric [Mo₆Cl₈(OC₉H₉)₆]²⁻ anions shown in Fig. 1. To a first approximation the clusters together with the sodium ions form PdCl₂-type chains which are arranged parallel to [010] to form a hexagonal-rod packing. The [Mo₆Cl₈]⁴⁺ core is coordinated by six terminal (*E*)-cinnamyl alcoholate ligands. Averaged values for $d_{Mo-Mo} = 2.607 \text{ \AA}$ and $d_{Mo-Cl} = 2.493 \text{ \AA}$ are comparable to those found for the Mo₆Cl₈⁴⁺ anion in salts with monovalent organic cations like tetrabutylammonium or tetraphenylphosphonium (Perchenek & Simon, 1990), indicating that exchange of the terminal halide for alcoholate ligands does not lead to major changes of the bonding relationships in the [Mo₆Cl₈]⁴⁺ unit; the averaged value for $d_{Mo-O} = 2.037 \text{ \AA}$ is similar to the one in [Mo₆Cl₈(OCH₃)₆]²⁻ (Chisholm, Heppert & Huffman, 1984). Individual bond lengths and angles are listed in Table 2.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54329 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

According to Fig. 2 the sodium ion is located in a distorted tetrahedron formed by two oxygen atoms of cluster-bonded (*E*)-cinnamyl alcoholate ligands, one nitrogen atom of a solvent acetonitrile or an oxygen atom of a solvent (*E*)-cinnamyl alcohol molecule, respectively. This disorder in the solvent coordination yields a simple explanation for the observed twofold disorder of the cluster-bonded alcoholate ligand which is nearest to those channels containing the disordered solvent molecules. The Mo—Mo distances in the cluster range from 2.596 (2) to 2.623 (2) Å. This differentiation of bond lengths is unexpected as the cluster has a closed-shell configuration with 24 electrons in metal—metal bonding states and should therefore be regular. Compounds containing distorted Mo₆ octahedra with 24 electrons have been reported before, e.g. Mo₆Cl₁₀Y (Y = S, Se, Te), with d_{Mo-Mo} in Mo₆Cl₁₀Se ranging from 2.598 (1) to 2.626 (1) Å (Perrin, Sargent, Le Traon & Le Traon, 1978). While the distortion of the Mo₆ octahedron in Mo₆Cl₁₀Se is obviously due to interconnection of the clusters *via* bridging atoms, no such explanation can be thought of for the molecular title compound.

References

- CHISHOLM, M. H., HEPPERT, J. A. & HUFFMAN, J. C. (1984). *Polyhedron*, **3**, 475–478.
 NANNELLI, P. & BLOCK, B. P. (1968). *Inorg. Chem.* **7**, 2423–2426.
 NANNELLI, P. & BLOCK, B. P. (1969). *Inorg. Chem.* **8**, 1767–1771.
 PERCHENEK, N. & SIMON, A. (1990). Unpublished results.
 PERRIN, C., SERGENT, M., LE TRAON, F. & LE TRAON, A. (1978). *J. Solid State Chem.* **25**, 197–204.
 SHELDRIK, G. M. (1988). *SHELXTL-Plus88 Structure Determination Software Programs*. Nicolet Instrument Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1991). **C47**, 2356–2358

Structure of Diaquabis(1,2-propanediamine)nickel(II) Dibromide Dihydrate

By M. R. DÍAZ, S. GARCÍA-GRANDA AND F. GÓMEZ-BELTRÁN

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

(Received 6 December 1990; accepted 11 June 1991)

Abstract. [Ni(C₃H₁₀N₂)₂(H₂O)₂]₂Br₂·2H₂O, $M_r = 438.83$, monoclinic, $P2_1/c$, $a = 7.510$ (9), $b = 16.264$ (6), $c = 7.632$ (3) Å, $\beta = 113.26$ (6)°, $V = 857$ (1) Å³, $Z = 2$, $D_x = 1.70 \text{ Mg m}^{-3}$, Mo $K\alpha$ radiation (graphite crystal monochromator, $\lambda = 0.71073 \text{ \AA}$), $\mu(\text{Mo } K\alpha) = 5.77 \text{ mm}^{-1}$, $F(000) = 444$,

$T = 293 \text{ K}$. Final conventional $R = 0.044$ for 943 observed reflections and 95 variables. The Ni—N distances, 2.106 (6) and 2.099 (6) Å, are typical for pseudo-octahedral coordination and the N—Ni—N bite angle is 83.3 (2)°. The Ni—N distances are slightly different due to the effect of the asymmetric C-substitution, showing a similar behaviour to the 2-methyl-1,2-propanediamine complexes.

* Address for correspondence.

Introduction. In the course of our investigations on transition-metal complexes, mainly Ni^{II} but also Cu^{II} and Co^{III}, with C-substituted ethylenediamines as ligands, we have reported several crystallographic studies on complexes within this series (García-Granda, Díaz, Barrio & Gómez-Beltrán, 1990; García-Granda, Díaz & Gómez-Beltrán, 1990b, 1991). Although many crystal structures of these complexes have been published, there is no report, as far as we know, of crystal structures of Ni^{II} complexes containing 1,2-propanediamine (pn) as the ligand, probably due to difficulties in crystallization. In order to explain the spectroscopic behaviour of these complexes, we have undertaken the crystal structure determination of a Ni^{II} complex with 1,2-propanediamine.

Experimental. Blue crystal, 0.01 × 0.16 × 0.23 mm. Mo K α radiation, graphite crystal monochromator, Enraf-Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions were determined from the angular settings of 25 reflections with $5 < \theta < 18^\circ$. Space group $P2_1/c$ from systematic absences. 2820 reflections were measured, hkl range $-10, 0, 0$ to $10, 22, 10$, $0 < \theta < 30^\circ$. ω - 2θ scan technique with a variable scan speed and a maximum scan time of 60 s per reflection. Intensity was checked by monitoring three standard reflections every 60 min. Final drift corrections were between 0.99 and 1.02. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction applied, using ψ scans (North, Phillips & Mathews, 1968), correction factors range from 0.54 to 1.50. Some doubly measured reflections were averaged, $R_{\text{int}} = 0.042$, 2479 unique reflections and 943 observed with $I > 3\sigma(I)$. Lorentz and polarization corrections applied and data reduced to $|F_o|$ values. Structure solved by Patterson interpretation using the program *SHELXS86* (Sheldrick, 1985) and Fourier synthesis. Isotropic least-squares refinement, using *SHELX76* (Sheldrick, 1976), converged to $R = 0.12$. At this stage an additional empirical absorption correction was applied (Walker & Stuart, 1983); the maximum and minimum absorption correction factors were 1.50 and 0.54, respectively. Further anisotropic refinements followed by a difference Fourier synthesis allowed the location of some H atoms, the rest were geometrically placed. Positional parameters and anisotropic thermal parameters for the non-H atoms were refined. All H atoms were refined isotropically with a common thermal parameter and riding as rigid groups on their parent atoms. The final conventional agreement factors were $R = 0.044$ and $wR = 0.046$ for the 943 observed reflections and 95 variables. Function minimized $\sum w(F_o - F_c)^2$, $w = 1/[\sigma^2(F_o) + 0.00080F_o^2]$ with $\sigma(F_o)$ from counting statistics. Maximum shift to e.s.d. ratio in

Table 1. *Fractional positional and thermal parameters with e.s.d.'s in parentheses*

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq} ($\text{\AA}^2 \times 10^2$)
Ni(1)	0.00000	0.00000	0.00000	3.18 (5)
Br(1)	0.3564 (1)	0.11362 (6)	0.5858 (1)	5.08 (4)
O(1)	0.2664 (8)	0.0645 (3)	0.1313 (7)	4.5 (2)
N(1)	-0.0771 (9)	0.0242 (4)	0.2320 (8)	3.9 (3)
N(2)	-0.147 (1)	0.1108 (4)	-0.1047 (8)	4.5 (3)
C(1)	-0.229 (1)	0.0908 (5)	0.172 (1)	4.9 (4)
C(2)	-0.176 (2)	0.1510 (5)	0.055 (1)	5.6 (4)
C(3)	-0.247 (2)	0.1296 (6)	0.347 (1)	6.4 (4)
O(2)	0.223 (1)	0.2004 (4)	0.904 (1)	6.8 (3)

Table 2. *Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses*

Ni(1)—O(1)	2.127 (5)	N(2)—C(2)	1.48 (1)
Ni(1)—N(1)	2.106 (5)	C(1)—C(2)	1.48 (1)
Ni(1)—N(2)	2.099 (6)	C(1)—C(3)	1.53 (1)
N(1)—C(1)	1.51 (1)		
O(1)—Ni(1)—N(1)	91.8 (2)	N(1)—C(1)—C(2)	108.0 (7)
O(1)—Ni(1)—N(2)	90.6 (2)	N(1)—C(1)—C(3)	110.4 (7)
N(1)—Ni(1)—N(2)	83.3 (2)	C(2)—C(1)—C(3)	113.0 (8)
Ni(1)—N(1)—C(1)	107.8 (4)	N(2)—C(2)—C(1)	111.7 (7)
Ni(1)—N(2)—C(2)	107.0 (5)		

the last full-matrix least-squares cycle was less than 0.004. Final difference Fourier map showed no peaks higher than 0.81 or deeper than -0.70 e \AA^{-3} . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). The plot was made with *PLUTO* (Motherwell & Clegg, 1978). Geometrical calculations were made with *PARST* (Nardelli, 1983). All calculations were made on a MicroVAX 3400 computer at the Scientific Computer Center of the University of Oviedo.

Discussion. Final atomic parameters and bond lengths and angles are given in Tables 1 and 2 respectively.* A *PLUTO* (Motherwell & Clegg, 1978) drawing of the complex cation giving the atomic numbering scheme is shown in Fig. 1. The central Ni atom is pseudo-octahedrally coordinated to two 1,2-propanediamine molecules and two water molecules in *trans* positions. The complex molecule is centrosymmetric, with the central Ni atom on a crystallographic center of symmetry. It is the first complex, within our series, of C-ethylenediamine derivatives and Ni^{II} with a bromide cation which exhibits pseudo-octahedral coordination (García-Granda,

* 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 54332 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

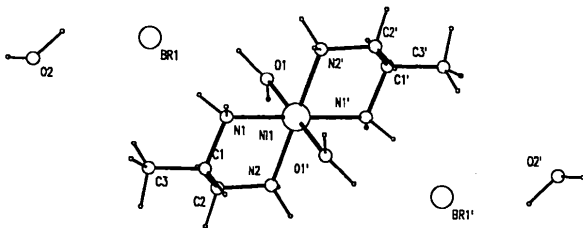


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) plot showing the anion-cation relationships, the Ni coordination and the atomic numbering scheme.

Díaz & Gómez-Beltrán, 1990*a,b*). The Ni—N distances, 2.106 (6) and 2.099 (6) Å, are typical for pseudo-octahedral coordination and the N—Ni—N bite angle is 83.3 (2)° which is close to the value 82.5 (2)° found for the Ni—2-methyl-1,2-propanediamine pseudo-octahedral complex (García-Granda & Gómez-Beltrán, 1984). It should be pointed out that the differences found in the N—Ni distances is the same effect as observed in the case of the 2-methyl-1,2-propanediamine complex. No unusual geometric features are present in the molecule. Weak hydrogen bonds are observed between the coordinated and uncoordinated water molecules and the bromide anions. The amino group N(2) is hydrogen bonded to the uncoordinated water molecule O(2) though

H(4). Water molecules, coordinated O(1) and uncoordinated O(2), are hydrogen bonded through H(5).

References

- GARCÍA-GRANDA, S., DÍAZ, M. R., BARRIO, C. & GÓMEZ-BELTRÁN, F. (1990). *Acta Cryst.* **C46**, 377–379.
 GARCÍA-GRANDA, S., DÍAZ, M. R. & GÓMEZ-BELTRÁN, F. (1990*a*). *Acta Cryst.* **C46**, 598–600.
 GARCÍA-GRANDA, S., DÍAZ, M. R. & GÓMEZ-BELTRÁN, F. (1990*b*). *Acta Cryst.* **C46**, 993–995, and references therein.
 GARCÍA-GRANDA, S., DÍAZ, M. R. & GÓMEZ-BELTRÁN, F. (1991). *Acta Cryst.* **C47**, 181–182.
 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.
 LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* **A30**, 580–584.
 MOTHERWELL, W. D. S. & CLEGG, W. (1978). *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). *SHELX76*. 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. (1991). **C47**, 2358–2362

Structure of the 1:4 Complex of Bis[1,2-oxalato(2-)]copper(II) and Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)

BY MINXIE QIAN, RAINER RUDERT AND PETER LUGER

Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-1000 Berlin 33, Germany

AND CHUANJIE GE AND XIAOHONG WANG

Institute of Chemistry, Academia Sinica Beijing, People's Republic of China

(Received 5 June 1990; accepted 11 June 1991)

Abstract. 4C₁₀H₈S₈·[Cu(C₂O₄)₂], *M_r* = 1778.20, triclinic, *P*1̄, *a* = 11.781 (2), *b* = 15.841 (3), *c* = 8.710 (2) Å, α = 91.15 (2), β = 94.00 (2), γ = 104.81 (1)°, *V* = 1567 (1) Å³, *Z* = 1, *D_x* = 1.884 Mg m⁻³, λ(Cu Kα) = 1.5406 Å, μ = 10.45 mm⁻¹, *F*(000) = 901, *T* = 295 K, *R* = 0.069 (*wR* = 0.066) for 4743 observed reflections. BEDT-TTF molecules form stacks along the *c* axis. The stacks are dimerized with the interplanar spacings being 3.674 (5) [(I)⋯(II)] and 3.926 (6) Å [(I)⋯(II')]. The interstack side-by-side S⋯S contact distances are in the range of 3.30 (1) to 3.593 (3) Å.

Introduction. In recent years a family of organic conductors based on BEDT-TTF has been synthesized. It includes the superconductor (BEDT-TTF)₂ReO₄ (*T_c* = 2 K at 0.4 GPa pressure) (Parkin, Engler, Schumaker, Lagier, Lee, Scott & Greene, 1983) and (BEDT-TTF)I₃ (*T_c* = 1.5 K at ambient pressure) (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984).

In many known BEDT-TTF salts the acceptor *X* is an anion with linear, planar, tetrahedral or octahedral geometry, such as I₃ (Leung, Emge, Beno, Wang