References

ANDERSSON, S. & JAGNER, S. (1985). *Acta Chem. Scand. Ser. A,* **39,** 297–305.

ASPLUND, M., JAGNER, S. & NILSSON, M. (1983). *Acta Chem. Scand. Ser. A,* **37,** 57–62.

BONDI, A. (1964). *J. Phys. Chem.* **68,** 441–451.

CLEGG, W., GARNER, C. D., NICHOLSON, J. R. & RAITHBY, P. R. (1983). *Acta Cryst.* **C39,** 1007–1009.

EMGE, T. J., LEUNG, P. C. W., BENO, M. A., WANG, H. H., FIRESTONE, M. A., WEBB, K. S., CARLSON, K. D., WILLIAMS, J. M., VENTURINI, E. L., AZEVEDO, L. J. & SCHIRBER, J. E. (1986). *Mol. Cryst. Liq. Cryst.* **132,** 363–383.

EMGE, T. J., WANG, H. H., BENO, M. A., LEUNG, P. C. W., FIRESTONE, M. A., JENKINS, H. C., COOK, J. D., CARLSON, K. D., WILLIAMS, J. M., VENTURINI, E. L., AZEVEDO, L. J. & SCHIRBER, J. E. (1985). *Inorg. Chem.* **24,** 1738–1740.

EMGE, T. J., WANG, H. H., LEUNG, P. C. W., RUST, P. R., COOK, J. D., JACKSON, P. L., CARLSON, K. D., WILLIAMS, J. M., WHANGBO, M.-H., VENTURINI, E. L., SCHIRBER, J. E., AZEVEDO, L. J. & FERRARO, J. R. (1986). *J. Am. Chem. Soc.* **108,** 695–702.

FRANCISCO, R. H. P., DE ALMEIDA SANTOS, R. H., LECHAT, J. R. & MASSABNI, A. C. (1981). *Acta Cryst.* B**37,** 232–234.

HUBER, C. P., POST, M. L. & SIIMAN, O. (1978). *Acta Cryst.* B**34,** 2629–2632.

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

KAISER, J., BRAUER, G., SCHRÖDER, F. A., TAYLOR, I. F. & RASMUSSEN, S. E. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1490–1493.

KOBAYASHI, H., KATO, R., KOBAYASHI, A., SAITO, G., TOKUMOTO, M., ANZAI, H. & ISHIGURO, T. (1986). *Chem. Lett.* pp. 89–92.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARSH, W. C. & TROTTER, J. (1971). *J. Chem. Soc. A,* pp. 1482–1486.

NEWTON, M. G., CAUGHMAN, H. D. & TAYLOR, R. C. (1970). *Chem. Commun.* p. 1227.

NEWTON, M. G., CAUGHMAN, H. D. & TAYLOR, R. C. (1974). *J. Chem. Soc. Dalton Trans.* pp. 258–264.

NILSSON, M. (1983). Private communication.

SAKURAI, T., KOBAYASHI, K., MASUDA, H., TSUBOYAMA, S. & TSUBOYAMA, K. (1983). *Acta Cryst.* C**39,** 334–337.

SIIMAN, O., HUBER, C. P. & POST, M. L. (1977). *Inorg. Chim. Acta,* **25,** L11–L14.

STROUSE, C. (1978). *UCLA Crystallographic Package.* Univ. of California, Los Angeles.

TSUBOYAMA, S., KOBAYASHI, K., SAKURAI, T. & TSUBOYAMA, K. (1984). *Acta Cryst.* C**40,** 1178–1181.

WANG, H. H., BENO, M. A., GEISER, U., FIRESTONE, M. A., WEBB, K. S., NUÑEZ, L., CRABTREE, G. W., CARLSON, K. D., WILLIAMS, J. M., AZEVEDO, L. J., KWAK, J. F. & SCHIRBER, J. E. (1985). *Inorg. Chem.* **24,** 2465–2466.

WHANGBO, M.-H. (1986). Private communication.

WILLIAMS, J. M., EMGE, T. J., WANG, H. H., BENO, M. A., COPPS, P. T., HALL, L. N., CARLSON, K. D. & CRABTREE, G. W. (1984). *Inorg. Chem.* **23,** 2558–2560.

WILLIAMS, J. M., WANG, H. H., BENO, M. A., EMGE, T. J., SOWA, L. M., COPPS, P. T., BEHROOZI, F., HALL, L. N., CARLSON, K. D. & CRABTREE, G. W. (1984). *Inorg. Chem.* **23,** 3839–3841.

YAGUBSKII, E. B., SHCHEGOLEV, I. F., LAUKHIN, V. N., KONONOVICH, P. A., KARTSOVNIK, M. W., ZVARYKINA, A. V. & BURAVOV, L. I. (1984). *Pis'ma Zh. Eksp. Teor. Fiz.* **39,** 12–15; *JETP Lett.* (English translation), **39,** 12–15.

Tetraaquabis(5-nitrotetrazolato-N^2)nickel(II)

BY J. CHARALAMBOUS, G. C. GEORGIOU AND K. HENRICK

School of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB, England

AND L. R. BATES AND M. HEALEY

*Royal Armament Research and Development Establishment (RARDE), Waltham Abbey, Essex EN9 1BP, England*

Abstract. $[Ni(CN_5O_2)_2(H_2O)_4]$, $M_r = 358 \cdot 8$, orthorhombic, $Cmca$, $a = 6 \cdot 872$ (2), $b = 16 \cdot 522$ (3), $c = 11 \cdot 900$ (3) Å, $V = 1351 \cdot 12$ Å^3, $Z = 4$, $D_x = 1 \cdot 76$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0 \cdot 71069$ Å, $\mu = 14 \cdot 17$ cm^{-1}, $F(000) = 728$, $T = 293$ K. Final $R = 0 \cdot 0471$ for 450 unique observed reflections. The Ni atom has octahedral coordination, site symmetry $2/m$ (C_{2h}), being bonded to two N atoms of different 5-nitrotetrazole rings in *trans* position [Ni—N = $2 \cdot 105$ (6) Å]; the nitro substituents are not involved in the bonding to the metal. The coordination is completed by four equatorial water molecules [Ni—O = $2 \cdot 125$ (5) Å].

Introduction. Complexes containing the anions of 5-substituted tetrazoles (see below) as ligands exhibit explosive properties (Butler, 1977), and some have been used as primers (McGuhan, 1979). The anions of 5-substituted tetrazoles are ambidentate and can coor-

dinate either through N(1) or N(2). Several studies of their complexes have indicated that the regiospecificity of coordination is sterically induced (Takach, Holt, Alcock, Henry & Nelson, 1980).
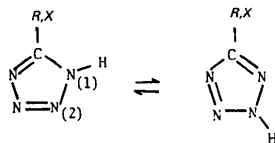
Experimental. Synthesis of the title compound was achieved by adding a stoichiometric amount of the hydrated sodium salt of 5-nitrotetrazole [Na(5-nt)].-$2H_2O$ (1·73 g, 10 mmol) in acetone (50 cm³) to a solution of nickel sulfate hexahydrate (1·31 g, 5 mmol) in water (25 cm³) and adjusting the pH to *ca* 8·5 with the dropwise addition of aqueous ammonia at 293 K. The crystals of the complex [Ni(5-nt)$_2$(H$_2$O)$_4$] were obtained by slow crystallization from acetone–water.

A fresh crystal of dimensions 0·38 × 0·32 × 0·24 mm was used in the study. 25 reflections used for measuring lattice parameters, $7 \le \theta \le 9°$. Intensity data were collected on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation and a scan width of 0·86°. A total of 459 unique reflections were examined in the 2θ range 3·0–25° of which 450 with $I/\sigma(I) > 3·0$ were used in subsequent stages, index range 0,0,0 to 8,19,14. Intensity measurements of standard reflections at 5 h intervals indicated no serious radiation damage of the crystal. Lorentz and polarization corrections were applied; no absorption correction was applied.

Solution of the Patterson map gave a site of $2/m$ symmetry for the Ni atom. Subsequent Fourier-difference syntheses gave the positions of all C, N, O and H atoms. Coordinates and anisotropic thermal parameters were refined for all non-H atoms in the final cycles of full-matrix least-squares refinement on F, with $w = 1/\sigma^2(F_o)$, yielding the final R of 0·0471 and wR of 0·0480. Maximum shift/e.s.d. value in final cycle, 0·007; in final difference map residual electron density within −0·4 and +0·8 e Å⁻³. *SHELX*76 (Sheldrick, 1976) was used, and the atomic scattering factors and corrections for the real and imaginary parts of anomalous dispersion are those given by Cromer & Mann (1968). The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.*

---

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond angles, intramolecular non-bonded distances and intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43548 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The atomic arrangement in the molecule is illustrated in Fig. 1, and the bond lengths and selected angles are given in Table 2. The Ni atom is six-coordinate, having a *trans* octahedral environment with two 5-nitrotetrazole rings bonded in a monodentate fashion and four water molecules.

The two 5-nitrotetrazole rings lie in the mirror plane and are related by the twofold axis. The coordination of the Ni atom is approximately octahedral with exact C_{2h} symmetry. The 5-nitrotetrazole rings are bonded through N(2) [Ni–N(2) 2·105 (6) Å]. The two C–N distances in the ring [C(1)–N(4) 1·320 (10) and C(1)–N(1) 1·305 (10) Å] are equal within experimental error. The N(3)–N(2) bond length of 1·308 (9) Å is significantly shorter than each of the other two N–N distances [N(3)–N(4) 1·345 (9) and N(1)–N(2) 1·338 (9) Å], consistent with greater localization of electron density in the former. The C–N and all the N–N bond distances are shorter than the normal single bonds given by Sutton (1958) (C–N 1·48, N–N

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²) with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Ni	0	0	0	0.0337 (7)
N(1)	0	0·1403 (4)	−0·1653 (6)	0.044 (4)
N(2)	0	0·0595 (4)	−0·1564 (5)	0.038 (4)
N(3)	0	0·0254 (3)	−0·2556 (6)	0.044 (4)
N(4)	0	0·0834 (4)	−0·3348 (5)	0.044 (4)
C(1)	0	0·1503 (4)	−0·2741 (6)	0.037 (4)
N(5)	0	0·2301 (5)	−0·3258 (8)	0.067 (6)
O(1)	0	0·2879 (4)	−0·2640 (9)	0.122 (8)
O(2)	0	0·2335 (4)	−0·4269 (6)	0.094 (6)
O(1w)	−0·2188 (8)	0·0804 (2)	0·0587 (4)	0.069 (3)

Table 2. *Bond lengths (Å) and angles (°)*

Ni–N(2)	2·105 (6)	Ni–O(1w)	2·125 (5)
N(1)–N(2)	1·338 (9)	N(1)–C(1)	1·305 (10)
N(2)–N(3)	1·308 (9)	N(3)–N(4)	1·345 (9)
N(4)–C(1)	1·320 (10)	C(1)–N(5)	1·454 (11)
N(5)–O(2)	1·204 (12)	N(5)–O(1)	1·205 (12)

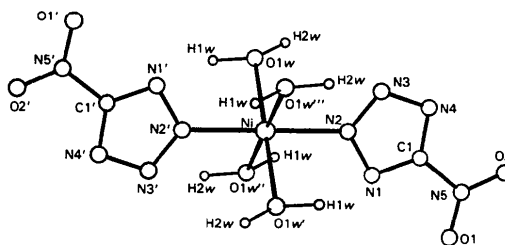|			
O(1w)–Ni–N(2)	89·9 (2)	N(2)–Ni–N(2')	180·0
O(1w)–Ni–O(1w'')	89·9 (3)	O(1w)–Ni–O(1w''')	90·1 (3)
O(1w)–Ni–N(2')	90·1 (2)	O(1w)–Ni–O(1w')	180·0

Fig. 1. Atomic arrangement in the molecule and numbering.

1·45 Å). These observations are comparable to the Cu complex of 5-(trifluoromethyl)tetrazole, where the metal is again bonded at the N(2) site (Gaughan, Bowman & Dori, 1972). The monodentate mode of bonding observed in the Ni complex contrasts the chelating and bridging character of the same ligand in mercuric 5-nitrotetrazolate, where there is coordination of the NO_2 group to the Hg atom (Huang, Jin, Shao, Wang & Zhu, 1982). The short intermolecular distance $H(1w)\cdots N(4)(-\frac{1}{2}-x, y, -\frac{1}{2}-z)$ (2·19 Å) is an indication of hydrogen bonding linking the complex molecules into infinite chains.

We acknowledge support for this work by the Procurement Executive, Ministry of Defence.

References

BUTLER, R. N. (1977). Adv. Heterocycl. Chem. 21, 323–435.
CROMER, D. T. & MANN, J. B. (1968). Acta Cryst. A24, 321–324.
GAUGHAN, A. P., BOWMAN, K. S. & DORI, Z. (1972). Inorg. Chem. 11, 601–608.
HUANG, H., JIN, X., SHAO, M., WANG, J. & ZHU, Y. (1982). Huaxue Tongbao, 6, 336–337, 368; Chem. Abstr. 97, 136922.
McGUHAN, R. (1979). Improvements in Primary Explosives Composition and Their Manufacture. Proc. 10th Symp. Explos. Pyrotechnics, San Diego.
SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.
SUTTON, L. E. (1958). Editor. Tables of Interatomic Distances and Configuration in Molecules and Ions. Spec. Publ. No. 11. London. The Chemical Society.
TAKACH, N. E., HOLT, E. M., ALCOCK, N. W., HENRY, R. A. & NELSON, J. H. (1980). J. Am. Chem. Soc. 102, 2968–2979.

Structure of Aqua[N,N'-bis(β-carbamoylethyl)-N-methyltrimethylenediamine]copper(II) Perchlorate Monohydrate*

BY TIAN-HUEY LU, CHIN-CHUN TSAI, MIN-SHIUN CHAO AND CHUNG-SUN CHUNG

National Tsing Hua University, Hsinchu, Taiwan 30043

Abstract. $[Cu(C_{10}H_{22}N_4O_2)(H_2O)](ClO_4)_2.H_2O$, $M_r = 528·8$, monoclinic, $P2_1/c$, $a = 10·195$ (2), $b = 14·245$ (4), $c = 14·372$ (5) Å, $\beta = 96·76$ (2)°, $V = 2072·5$ Å^3, $Z = 4$, $D_x = 1·695$, $D_m = 1·687$ Mg m^{-3}, $\lambda(Mo K\alpha) = 0·7093$ Å, $\mu = 1·38$ mm^{-1}, $F(000) = 1094·7$, $T = 297$ (5) K. Final $R = 0·064$ for 1513 significant reflections. The Cu atom is five-coordinate in a slightly distorted square-pyramidal geometry, and is displaced 0·9 Å from the best plane of the two amino N atoms and the two amide O atoms toward the apex of the pyramid, which is occupied by a water O atom with the Cu–O distance 2·38(2)Å. Two of the three six-membered rings are in chair forms and the other is in a twist form. Hydrogen bonds play an important role in the crystal structure.

Introduction. In a previous paper we have reported the crystal structure of aqua[N,N'-bis(β-carbamoylethyl)-trimethylenediamine]perchloratocopper(II) perchlorate monohydrate, [Cu(ClO$_4$)(bctn)(H$_2$O)]ClO$_4$.H$_2$O (Hong, Lee, Lee, Chao & Chung, 1987). In this work, the crystal structure of aqua[N,N'-bis(β-carbamoylethyl)-N-methyltrimethylenediamine]copper(II) perchlorate monohydrate, [Cu(N-CH$_3$bctn)(H$_2$O)](ClO$_4$)$_2$.H$_2$O, has been determined.

---

* Aqua(4-methyl)-4,8-diazaundecanediamide)copper(II) diperchlorate monohydrate.

Experimental. The N-CH$_3$bctn ligand was prepared as follows: 13·6 ml (0·2 mol) of N-methyltrimethylenediamine and 28·4 g (0·4 mol) of acrylamide in 80 ml acetonitrile were refluxed for 2 h. The solution was cooled and the product, N-CH$_3$bctn, filtered off. These crystals were washed with chloroform, m.p. 328–329 K (found: C, 51·6; H, 9·51; N, 23·8%; calculated for C$_{10}$H$_{22}$N$_4$O$_2$: C, 52·1; H, 9·63; N, 24·3%), recrystallized from chloroform, and dried in air. N-CH$_3$bctn was reacted with Cu(ClO$_4$)$_2$.6H$_2$O in water. Blue [Cu(N-CH$_3$bctn)(H$_2$O)](ClO$_4$)$_2$.H$_2$O was crystallized from absolute alcohol.

Density measured by flotation. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; a crystal of about 0·2 × 0·3 × 0·2 mm was cut for data collection, unit-cell parameters from 25 reflections with 20 < $2\theta < 28°$, data collected by ω–2θ scans with scan width of 2 × (0·9 + 0·35tanθ)° and scan speed of $\frac{20}{3}$–$\frac{20}{16}$° min^{-1}, standard reflections 017, 0$\bar{1}$7 and 01$\bar{7}$ checked every 2 h, varied within 2$\sigma(I)$. Max. (sinθ)/λ = 0·66 Å^{-1} (−12 ≤ h ≤ 13, 0 ≤ k ≤ 18, 1 ≤ l ≤ 18), 4983 reflections collected, 1513 significant with $I >$ 2·5$\sigma(I)$. Empirical absorption correction based on azimuthal rotation from three reflections (004, 0$\bar{1}$7, $\bar{1}$08) (North, Phillips & Mathews, 1968); the minimum, maximum and average correction factors are 0·8817, 0·9994 and 0·9329, respectively. Heavy atom Cu was located by using Patterson synthesis. Other atom