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# Structure Determination of a Nickel Croconate Complex: $[Ni(OH_2)(C_5O_5)(C_3H_4N_2)_3]H_2O$


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**Abstract.** Aqua(4,5-dihydroxy-4-cyclopentene-1,2,3-trionato)tris(imidazole)nickel(II) monohydrate, $C_{14}H_{14}N_6NiO_6.H_2O$, $M_r = 439{\cdot}0$, monoclinic, $P2_1/c$, $a = 8{\cdot}581$ (1), $b = 9{\cdot}442$ (1), $c = 22{\cdot}583$ (2) Å, $\beta = 93{\cdot}06$ (1)°, $V = 1827{\cdot}1$ (7) Å$^3$, $Z = 4$, $D_x = 1{\cdot}596$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}11$ mm$^{-1}$, $F(000) = 904$, $T = 293$ K. Full-matrix least-squares refinement based on 2761 reflections led to $R$ and $wR$ values of 0·034 and 0·037 respectively. The coordination of the metal is ensured by three imidazole groups, one water molecule and one croconate molecule acting as chelating ligand.


**Experimental.** Blue-green parallelepiped crystals obtained from reaction in water of $NiCl_2$, $6H_2O$ (0·5 mmol), imidazole (0·5 mmol) and sodium croconate $C_5O_5Na_2$, $3H_2O$ (0·25 mmol). Analysis: calculated C 38·30, H 3·67, N 19·14%; found C 37·91, H 3·37, N 18·66%. Crystal 0·40 × 0·075 × 0·05 mm, sealed on a glass fiber, CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, cell parameters from a least-squares fitting of 25 reflections with $\theta$ between 7·2 and 14·7°, 4215 reflections measured, using $\omega/2\theta$ scan for $2\theta$ from 3 to 54° ($h$ 0 to 10, $k$ 0 to 12, $l$ −28 to 28), scan range $(0{\cdot}90 + 0{\cdot}35\tan\theta)°$. Intensities of three reflections (008, 040, 304) measured every 2 h during data collection showed a decay of 5%. Corrections for Lp and linear decay. Empirical absorption corrections (North, Phillips & Mathews, 1968): $T_{min} = 0{\cdot}90$, $T_{max} = 1{\cdot}00$ and merging equivalent reflections $0kl$ and $0k\bar{l}$; $R_{int} = 0{\cdot}019$. Heavy-atom method followed by Fourier and least-squares techniques using 2761 reflections having $F_o^2 > 2\sigma(F_o^2)$ based on counting statistics. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, with anisotropic thermal parameters for all non-H atoms, all H atoms observed on a Fourier difference map, H atoms from water molecules allowed to vary, other H atoms in constrained geometry (C—H = N—H = 0·97 Å).

Isotropic $U_H$ allowed to vary (one for each H from the water molecule, one for all other H atoms). $R = 0{\cdot}034$, $wR = 0{\cdot}037$, 268 variables, unit weights.† Mean and max. parameter shifts $0{\cdot}009\sigma$ and $0{\cdot}078\sigma$, respectively. Max. and min. height in final $\Delta F$ map 0·79 and −0·36 e Å$^{-3}$. Scattering factors including real and imaginary parts of anomalous dispersion from *International Tables for X-ray Crystallography* (1974, Vol IV, pp. 99–101, 149) and from Stewart, Davidson & Simpson (1965) for H atoms.

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† Lists of structure factors, anisotropic thermal parameters least-squares-planes equations and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53432 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic temperature factors* ($Å^2 \times 10^2$) *with e.s.d.'s in parentheses*

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Ni | 0·34669 (4) | 0·60758 (5) | 0·62036 (2) | 2·63 (6) |
| Ow(1) | 0·3486 (2) | 0·3911 (3) | 0·6007 (1) | 3·4 (4) |
| Ow(2) | 0·8118 (5) | 0·9641 (5) | 0·5586 (2) | 8·6 (9) |
| O(1) | 0·1159 (2) | 0·6145 (3) | 0·58019 (9) | 3·1 (4) |
| O(2) | 0·4030 (2) | 0·6479 (3) | 0·5295 (1) | 3·6 (4) |
| O(3) | 0·3476 (3) | 0·7308 (3) | 0·4020 (1) | 3·9 (4) |
| O(4) | 0·0153 (3) | 0·7655 (4) | 0·3821 (1) | 4·7 (5) |
| O(5) | −0·1390 (2) | 0·6866 (3) | 0·4905 (1) | 3·0 (4) |
| N(1) | 0·5802 (3) | 0·5950 (3) | 0·6446 (1) | 3·0 (4) |
| N(2) | 0·8314 (3) | 0·5947 (4) | 0·6360 (1) | 4·1 (5) |
| N(3) | 0·2649 (3) | 0·5659 (3) | 0·7027 (1) | 2·7 (4) |
| N(4) | 0·1860 (4) | 0·5984 (5) | 0·7925 (1) | 5·8 (7) |
| N(5) | 0·3363 (4) | 0·8246 (3) | 0·6307 (1) | 3·4 (5) |
| N(6) | 0·2513 (5) | 1·0488 (4) | 0·6279 (2) | 5·8 (7) |
| C(1) | 0·1260 (3) | 0·6511 (4) | 0·5261 (2) | 2·7 (5) |
| C(2) | 0·2765 (4) | 0·6684 (3) | 0·5006 (2) | 2·7 (5) |
| C(3) | 0·2525 (3) | 0·7080 (4) | 0·4390 (1) | 2·7 (5) |
| C(4) | 0·0801 (3) | 0·7243 (4) | 0·4281 (2) | 3·1 (5) |
| C(5) | 0·0055 (4) | 0·6863 (3) | 0·4834 (1) | 2·8 (5) |
| C(6) | 0·6905 (3) | 0·6139 (4) | 0·6076 (2) | 3·3 (5) |
| C(7) | 0·8082 (4) | 0·5585 (5) | 0·6935 (2) | 4·6 (7) |
| C(8) | 0·6496 (4) | 0·5615 (5) | 0·6981 (2) | 4·0 (6) |
| C(9) | 0·2422 (5) | 0·6629 (5) | 0·7443 (2) | 4·7 (7) |
| C(10) | 0·1749 (5) | 0·4564 (6) | 0·7806 (2) | 5·2 (8) |
| C(11) | 0·2203 (4) | 0·4393 (4) | 0·7254 (2) | 3·9 (6) |
| C(12) | 0·2121 (5) | 0·9112 (5) | 0·6225 (2) | 5·5 (8) |
| C(13) | 0·4062 (5) | 1·0524 (5) | 0·6393 (2) | 6·4 (9) |
| C(14) | 0·4520 (5) | 0·9169 (5) | 0·6420 (2) | 6·1 (9) |
| H1(Ow1) | 0·283 (3) | 0·362 (4) | 0·568 (1) | 6·1 (4) |
| H2(Ow1) | 0·442 (3) | 0·337 (4) | 0·602 (2) | 6·1 (4) |
| H1(Ow2) | 0·812 (7) | 0·866 (4) | 0·533 (2) | 8·4 (6) |
| H2(Ow2) | 0·863 (7) | 1·023 (4) | 0·540 (2) | 8·4 (6) |
| H(N2) | 0·932 | 0·605 | 0·619 | 6·0 (4) |
| H(N4) | 0·159 | 0·645 | 0·829 | 6·0 (4) |
| H(N6) | 0·181 | 1·129 | 0·624 | 6·0 (4) |
| H(C6) | 0·674 | 0·638 | 0·566 | 6·0 (4) |
| H(C7) | 0·887 | 0·536 | 0·724 | 6·0 (4) |
| H(C8) | 0·596 | 0·543 | 0·734 | 6·0 (4) |
| H(C9) | 0·263 | 0·764 | 0·741 | 6·0 (4) |
| H(C10) | 0·141 | 0·383 | 0·807 | 6·0 (4) |
| H(C11) | 0·222 | 0·350 | 0·705 | 6·0 (4) |
| H(C12) | 0·106 | 0·878 | 0·614 | 6·0 (4) |
| H(C13) | 0·471 | 1·136 | 0·645 | 6·0 (4) |
| H(C14) | 0·559 | 0·889 | 0·651 | 6·0 (4) |

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

| | | | |
|---|---|---|---|
| Ni—N(1) | 2·052 (2) | Ni—O(1) | 2·135 (2) |
| Ni—N(3) | 2·061 (3) | Ni—O(2) | 2·166 (2) |
| Ni—N(5) | 2·065 (3) | Ni—Ow(1) | 2·091 (3) |
| N(1)—C(6) | 1·308 (4) | C(13)—C(14) | 1·339 (7) |
| C(6)—N(2) | 1·350 (4) | C(14)—N(5) | 1·335 (5) |
| N(2)—C(7) | 1·368 (5) | C(1)—O(1) | 1·276 (4) |
| C(7)—C(8) | 1·371 (5) | C(2)—O(2) | 1·252 (4) |
| C(8)—N(1) | 1·356 (4) | C(3)—O(3) | 1·218 (4) |
| N(3)—C(9) | 1·333 (5) | C(4)—O(4) | 1·215 (4) |
| C(9)—N(4) | 1·359 (5) | C(5)—O(5) | 1·259 (4) |
| N(4)—C(10) | 1·370 (7) | C(1)—C(2) | 1·452 (4) |
| C(10)—C(11) | 1·336 (5) | C(2)—C(3) | 1·444 (5) |
| C(11)—N(3) | 1·363 (5) | C(3)—C(4) | 1·495 (4) |
| N(5)—C(12) | 1·348 (5) | C(4)—C(5) | 1·479 (5) |
| C(12)—N(6) | 1·346 (6) | C(5)—C(1) | 1·416 (4) |
| N(6)—C(13) | 1·340 (6) | | |
| | | | |
| N(1)—Ni—N(3) | 97·1 (1) | N(4)—C(10)—C(11) | 106·3 (4) |
| N(1)—Ni—N(5) | 94·3 (1) | C(10)—C(11)—O(3) | 110·3 (4) |
| N(1)—Ni—O(1) | 170·2 (1) | Ni—N(5)—C(12) | 128·7 (3) |
| N(1)—Ni—O(2) | 89·92 (9) | Ni—N(5)—C(14) | 129·3 (3) |
| N(1)—Ni—Ow(1) | 88·9 (1) | C(12)—N(5)—C(14) | 101·8 (3) |
| N(3)—Ni—N(5) | 93·9 (1) | N(5)—C(12)—N(6) | 112·4 (4) |
| N(3)—Ni—O(1) | 92·08 (9) | C(12)—N(6)—C(13) | 106·4 (4) |
| N(3)—Ni—O(2) | 172·87 (8) | N(6)—C(13)—C(14) | 106·7 (4) |
| N(3)—Ni—Ow(1) | 90·7 (1) | C(13)—C(14)—N(5) | 113·6 (4) |
| N(5)—Ni—O(1) | 88·4 (1) | Ni—O(1)—C(1) | 107·8 (2) |
| N(5)—Ni—O(2) | 86·9 (1) | Ni—O(2)—C(2) | 106·9 (2) |
| N(5)—Ni—Ow(1) | 174·0 (1) | O(1)—C(1)—C(5) | 129·1 (3) |
| O(1)—Ni—O(2) | 80·86 (8) | O(1)—C(1)—C(2) | 121·2 (3) |
| O(1)—Ni—Ow(1) | 87·55 (9) | C(5)—C(1)—C(2) | 109·6 (3) |
| O(2)—Ni—Ow(1) | 88·1 (1) | O(2)—C(2)—C(1) | 122·6 (3) |
| Ni—N(1)—C(6) | 123·5 (2) | O(2)—C(2)—C(3) | 128·2 (3) |
| Ni—N(1)—C(8) | 128·9 (2) | C(1)—C(2)—C(3) | 109·2 (3) |
| C(6)—N(1)—C(8) | 107·6 (3) | O(3)—C(3)—C(2) | 129·8 (3) |
| N(1)—C(6)—N(2) | 109·8 (3) | O(3)—C(3)—C(4) | 124·2 (3) |
| C(6)—N(2)—C(7) | 108·2 (3) | C(2)—C(3)—C(4) | 105·9 (3) |
| N(2)—C(7)—C(8) | 105·2 (3) | O(4)—C(4)—C(3) | 125·3 (3) |
| C(7)—C(8)—N(1) | 109·1 (3) | O(4)—C(4)—C(5) | 126·9 (3) |
| Ni—N(3)—C(9) | 125·0 (3) | C(3)—C(4)—C(5) | 107·8 (3) |
| Ni—N(3)—C(11) | 128·5 (2) | O(5)—C(5)—C(4) | 125·5 (3) |
| C(9)—N(3)—C(11) | 106·5 (3) | O(5)—C(5)—C(1) | 127·0 (3) |
| N(3)—C(9)—N(4) | 109·1 (4) | C(4)—C(5)—C(1) | 107·4 (3) |
| C(9)—N(4)—C(10) | 107·8 (3) | | |
| | | | |
| Water Molecules | | | |
| Ow(1)—H1(Ow1) | 0·95 (3) | Ow(1)—H2(Ow1) | 0·95 (3) |
| Ow(2)—H1(Ow2) | 0·95 (4) | Ow(2)—H2(Ow2) | 0·95 (5) |
| | | | |
| Ni—Ow(1)—H1(Ow1) | 116· (2) | Ni—Ow(1)—H2(Ow1) | 123· (2) |
| H1(Ow1)—Ow(1)—H2(Ow1) | 110· (3) | H1(Ow2)—Ow(2)—H2(Ow2) | 109· (4) |
| | | | |
| Hydrogen Bonds | | | |
| Ow(1)···O(5$^{ii}$) | 2·761 (3) | Ow(1)···O(3$^{iii}$) | 2·854 (3) |
| H1(Ow1)···O(5$^{ii}$) | 1·82 (3) | H2(Ow1)···O(3$^{iii}$) | 1·92 (2) |
| | | | |
| Ow(2)···O(5$^{i}$) | 2·935 (5) | N(2)···O(1$^{i}$) | 2·813 (3) |
| H1(Ow2)···O(5$^{i}$) | 2·00 (4) | H(N2)···O(1$^{i}$) | 1·85 |
| | | | |
| N(4)···O(4$^{v}$) | 2·865 (4) | N(6)···O(4$^{iv}$) | 2·882 (5) |
| H(N4)···O(4$^{v}$) | 1·96 | H(N6···O(4$^{iv}$) | 1·96 |
| | | | |
| Ow(1)—H1(Ow1)···O(5$^{ii}$) | 174· (3) | Ow(1)—H2(Ow1)···O(3$^{iii}$) | 166· (3) |
| Ow(2)—H1(Ow2)···O(5$^{i}$) | 166· (5) | N(2)—H(N2)···O(1$^{i}$) | 175· |
| N(4)—H(N4)···O(4$^{v}$) | 155· | N(6)—H(N6)···O(4$^{iv}$) | 159· |

Symmetry operations: (i) $1+x, y, z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 2-y, 1-z$; (v) $x, \frac{3}{2}-y, \frac{1}{2}+z$.

VAX 730 computer, programs: *SDP* (B. A. Frenz & Associates, Inc., 1985), *SHELX*76 (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964) and *NRC* (Ahmed, Hall, Pippy & Huber, 1966).

**Related literature.** The final positional and equivalent isotropic thermal parameters are listed in Table 1. The thermal-ellipsoid plot of the molecule (Johnson, 1965) is shown in Fig. 1 with the atomic numbering. The packing of the molecules in the unit cell is shown in Fig. 2 with the hydrogen-bonding scheme. The packing is enhanced by strong hydrogen bonds between the croconate anion or the imidazole ligand and the coordinated water and the water of crystallization molecules. Bond lengths and angles are listed in Table 2.

The anion of croconic acid isolated as early as 1825 by Gmelin (1825) has more recently been the object of theoretical and experimental studies. It was recognized as a member of the cyclic $(CO)_n$ aromatic series which is stabilized by delocalization of $\pi$ electrons over all the ring. West & Niu (1963) have prepared a series of divalent transition-metal salts of general formula $(C_5O_5)M(OH_2)_3$ (where $M$ = Mn, Fe, Co, Ni or Cu) which from similar X-ray powder patterns appear to be isostructural. In this paper we report the crystal structure of a nickel complex involving croconic acid and imidazole.

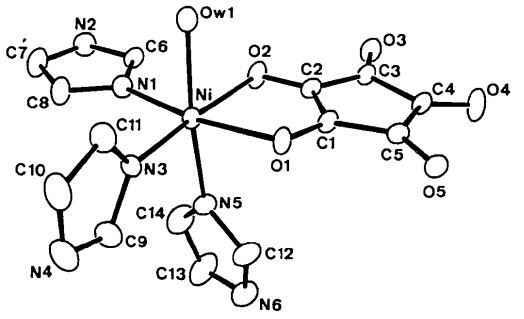


Fig. 1. *ORTEP* plot showing 30% probability thermal ellipsoids.

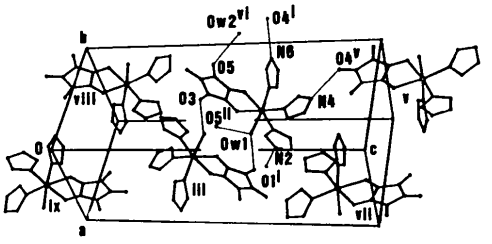


Fig. 2 An *ORTEP* view of the unit-cell contents with hydrogen-bonding scheme (fine lines). Symmetry operations are: (i) $1+x, y, z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1-y, 1-z$; (v) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (vi) $1+x, y, z$; (vii) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (viii) $x, \frac{3}{2}-y, -\frac{1}{2}+z$; (ix) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

The metal atom is surrounded by a croconate molecule acting as chelating ligand, three imidazole molecules and one water molecule. In nickel croconate itself (Bottei, Chang & Lusardi, 1979) the complex is a one-dimensional polymer with the infinite chain resulting from the bonding of each metal to two adjacent O atoms of one croconate and to a single oxygen atom of a second croconate molecule such that each croconate is three-coordinated.

In this compound, croconate is only two-coordinated as chelating nickel. The croconate ligand is planar although the C—C bond lengths suggest a partial localization of the $\pi$ electrons. The C(5)—C(1) bond [1·416 (4) Å] is shorter than the other bonds in the ring [1·495 (4) to 1·444 (5) Å]. The Ni—N bonds are quite similar and it is not possible to discriminate between in plane and out of plane. The geometry of the imidazole ligand is similar to that reported earlier (Henrikson, 1977).

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# The Room- and Low-Temperature Structures of $(\varphi_4As)CuCl_3$, an Isolated, Non-Planar $Cu_2Cl_6^{2-}$ Ion


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**Abstract.** Tetraphenylarsonium trichlorocuprate(II), $[As(C_6H_5)_4][CuCl_3]$, $M_r = 553·2$, monoclinic, $P2_1/n$, $Z = 4$, Cu $K\alpha$ ($\lambda = 1·54178$ Å), $F(000) = 1108·0$. The room-temperature structure (RT) has $a = 9·289$ (3), $b = 19·577$ (6), $c = 13·464$ (5) Å, $\beta = 108·89$ (2)°, $V = 2317$ (1) Å$^3$, $D_x = 1·58$ g cm$^{-3}$, $\mu = 63$ cm$^{-1}$, $R = 0·0474$ for 2154 unique observed $[I \geq 3\sigma(I)]$ reflections and 214 parameters. The low-temperature, 113 K, structure (LT) has $a = 9·220$ (3), $b = 19·494$ (5), $c = 13·222$ (4) Å, $\beta = 108·65$ (2)°, $V = 2252$ (1) Å$^3$, $D_x = 1·63$ g cm$^{-2}$, $\mu = 64$ cm$^{-1}$, $R = 0·0461$ for 2155 unique observed $[I \geq 3\sigma(I)]$ reflections and 214 parameters. At both temperatures, the $[Cu_2Cl_6]^{2-}$ ion is isolated, with Cu atom geometries


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