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

| | | | |
|---|---|---|---|
| Ni–N(1) | 2·094 (2) | C(1)–N(2) | 1·334 (3) |
| Ni–N(3) | 2·164 (2) | C(4)–N(4) | 1·347 (3) |
| Ni–N(5) | 2·063 (2) | C(2)–N(3) | 1·473 (3) |
| C(1)–C(2) | 1·510 (3) | C(3)–N(3) | 1·478 (3) |
| C(3)–C(4) | 1·502 (3) | N(1)–O(1) | 1·430 (2) |
| C(1)–N(1) | 1·290 (3) | N(5)–O(2) | 1·424 (2) |
| C(4)–N(5) | 1·290 (3) | | |
| N(oxime)–Ni–N(amine) | | C(2)–C(1)–N(2) | 118·4 (2) |
| Intrachelate | | C(1)–C(2)–N(3) | 110·0 (2) |
| N(5)–Ni–N(3) | 79·33 (7) | C(4)–C(3)–N(3) | 113·1 (2) |
| N(1)–Ni–N(3) | 76·00 (6) | C(3)–C(4)–N(4) | 116·3 (2) |
| Interchelate | | C(3)–C(4)–N(5) | 118·1 (2) |
| N(5)–Ni–N(3$^{i}$) | 168·83 (7) | N(4)–C(4)–N(5) | 125·6 (2) |
| N(1$^{i}$)–Ni–N(3) | 93·89 (6) | Ni–N(5)–C(4) | 118·2 (1) |
| N(oxime)–Ni–N(oxime) | | Ni–N(3)–C(2) | 107·6 (1) |
| Intrachelate | | Ni–N(3)–C(3) | 110·5 (1) |
| N(1)–Ni–N(5) | 95·68 (7) | C(2)–N(3)–C(3) | 111·4 (2) |
| Interchelate | | Ni–N(1)–C(1) | 117·9 (1) |
| N(5$^{i}$)–Ni–N(5) | 105·76 (7) | Ni–N(1)–O(2) | 130·5 (1) |
| N(1$^{i}$)–Ni–N(1) | 164·83 (6) | Ni–N(5)–O(2) | 130·7 (1) |
| N(1$^{i}$)–Ni–N(5) | 93·46 (7) | C(4)–N(5)–O(2) | 110·6 (2) |
| N(3)–Ni–N(3$^{i}$) | 95·48 (7) | C(1)–N(1)–O(1) | 110·5 (2) |
| C(2)–C(1)–N(1) | 115·4 (2) | N(1)–C(1)–N(2) | 126·1 (2) |

Symmetry code: (i) $-x, y, \frac{3}{2}-z$.

Table 3. *Hydrogen bonds in cis-facial* [Ni(*ibo*)$_2$]Cl$_2$

| Type $A$–H···$B$ | $A$ | H | $B$ | Distance (Å) $A$–$B$ | $A$–H | H–$B$ | Angle (°) $A$–H–$B$ |
|---|---|---|---|---|---|---|---|
| N–H···Cl | N(3)amine | H(6) | Cl | 3·391 (2) | 0·88 (2) | 2·53 (2) | 168 (2) |
| | N(2)amide | H(2) | Cl | 3·283 (3) | 0·84 (3) | 2·55 (3) | 146 (3) |
| | N(4)amidc | H(9) | Cl | 3·338 (2) | 0·88 (2) | 2·61 (3) | 142 (3) |
| O–H···Cl | O(2)oxime | H(11) | Cl | 3·181 (2) | 0·78 (3) | 2·41 (3) | 167 (3) |
| | O(1)oxime | H(1) | Cl | 3·072 (2) | 0·78 (3) | 2·30 (3) | 169 (3) |
| N–H···O | N(4)amide | H(9) | O(2) | 2·584 (3) | 0·79 (3) | 2·27 (3) | 101 (2) |
| | N(2)amide | H(3) | O(1) | 2·590 (3) | 0·86 (3) | 2·23 (3) | 106 (2) |
| | N(4)amide | H(10) | O(1) | 2·996 (3) | 0·79 (3) | 2·20 (3) | 175 (3) |

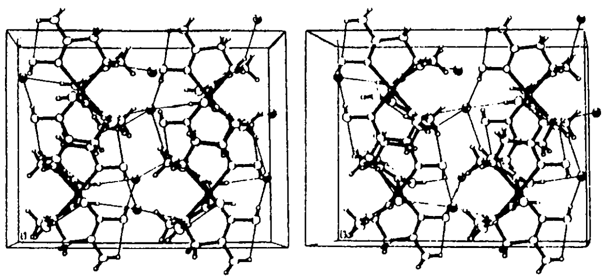

Fig. 2. Packing diagram (50% probability ellipsoids). A stereoview down the *b* axis of the *ac* plane with the origin at left back corner and the *c* axis vertical, shaded ellipsoids for the Ni and Cl atoms; the narrow lines depict the rather extensive hydrogen bonding.

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*Acta Cryst.* (1985). C**41**, 1031–1033

# Structure of a Fully Conjugated Macrocyclic Complex: (1,4,8,11-Tetraazacyclotetradeca-2,4,6,9,11,13-hexaene-2,3,9,10-tetracarbonitrilato)nickel(II), [Ni($C_{14}H_6N_8$)]

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(*Received* 18 *December* 1984; *accepted* 4 *March* 1985)

**Abstract.** $M_r = 344·95$, monoclinic, $C2/m$, $a = 13·674$ (3), $b = 14·469$ (4), $c = 3·7696$ (8) Å, $\beta = 96·55$ (2)°, $V = 740·95$ Å$^3$, $Z = 2$, $D_m = 1·57$, $D_x = 1·55$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7093 Å, $\mu = 1·324$ mm$^{-1}$, $F(000) = 348$, $T = 298$ K, final $R = 0·042$ for 879 observed reflections. The complex molecule is nearly planar and has crystallographic $2/m$ symmetry. The molecules are packed in a parallel fashion along the $c$ axis with a close interplanar distance of 3·357 (3) Å. The bond pattern of the macrocyclic ligand in the complex consists of a delocalized six-membered ring and a five-membered ring with a localized C=C double bond linked by two single C–N bonds.

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**Introduction.** The transition-metal complexes with unsaturated electron-rich ligands have unusual properties, such as spectroscopic, magnetic, and redox properties. The extent of $\pi$-electron delocalization over the unsaturated electron-rich ligand moiety is also a novel structural property. Examples of this type are metal complexes of dithiene (Teo & Snyder-Robinson, 1979), *o*-benzoquinone diimine anion (Hall & Soderberg, 1968; Christoph & Goedken, 1973), diiminosuccinonitrilato anion (Peng, Wang & Chiang, 1984; Peng, Liaw, Wang & Simon, 1985) and a fully conjugated 14-membered macrocyclic ligand (Peng & Goedken, 1976; Weiss, Gordon & Goedken, 1977).

The title complex was synthesized by the metal template reaction of diaminomaleonitrile with 1,1,3,3-tetraethoxypropane and nickel(II) acetate (Kohlmeyer, Lorch, Bauer & Breitmaier, 1978). The structure was determined in order to elucidate the structural properties of the title 14-membered macrocyclic ligand.

**Experimental.** Crystals of $[Ni(C_{14}H_6N_8)]$ obtained by slow cooling of saturated DMF solution. Needle crystal 0·1 × 0·1 × 0·6 mm. CAD-4 diffractometer. $D_m$ measured by flotation (mixed solution of $CCl_4$ and $CHCl_3$). Absorption correction according to the experimental $\psi$ rotation. $2\theta_{max} = 60°$ $(-19 \le h \le 19,$ $0 \le k \le 20,$ $0 \le l \le 5)$. Unit cell: least-squares refinement of 20 reflections $(15° < 2\theta < 25°)$. Three standard reflections, variation <2%. 1122 total reflections measured, 879 with $I \ge 2\sigma(I)$. $R = 0{\cdot}042$, $wR = 0{\cdot}031$, $S = 1{\cdot}45$ based on $F$. $w = 1/\sigma^2(F_o)$. Structure obtained by Fourier synthesis with Ni atom at $2/m$. H atoms found on difference Fourier synthesis were refined by least-squares process. Non-H atoms anisotropic, H atoms isotropic. $(\Delta/\sigma)_{max} = 0{\cdot}08$. Peaks on final $\Delta\rho$ map $\le |0{\cdot}3|$ e Å$^{-3}$. Secondary-extinction coefficient 0·279 (length in µm). Atomic scattering factors calculated by the analytical form using the coefficients in *International Tables for X-ray Crystallography* (1974). Programs from NRCC *PDP*-11 package (Gabe & Lee, 1981).

**Discussion.** Atomic positional parameters and equivalent isotropic temperature factors are listed in Table 1.* The bond lengths and angles are given in Fig. 1. The title complex is planar with a maximum deviation of 0·122 (3) Å [N(1)] from the plane formed by the Ni atom and the four donor N atoms. The molecule can be described as having approximate $D_{2h}$ symmetry.

The macrocyclic complex contains delocalized six-membered propane-1,3-diimino chelate rings, comparing well with those in $[Ni(C_{18}H_{14}N_4)]$ (Weiss, Gordon & Goedken, 1977) (1·343 and 1·375 *vs* 1·327 and 1·384 Å). In the five-membered chelate rings, the bond pattern of the complex is very similar to that of diaminomaleonitrile (damn) (Penfold & Lipscomb, 1961) (1·360 and 1·397 *vs* 1·363 and 1·392 Å) which has a localized C=C double-bond arrangement. It is different from that of $[Ni(disn)_2]$ (disn = diiminosuccinonitrilato) which has a delocalized electronic state (Peng, Wang & Chiang, 1984) (1·360 and 1·397 *vs* 1·403 and 1·331 Å). From the structure determination, we can conclude that the bond pattern of the essentially planar macrocyclic ligand is such that it includes a delocalized propane-1,3-diimino six-membered chelate ring and a five-membered chelate ring with the localized C=C double bond linked by two nominally single C—N bonds. Selected bond distances and angles of a few similar structures are listed in Table 2.

The authors would like to express their appreciation for the support of this work by the National Science Council.

Table 1. *Fractional atomic coordinates and $B_{eq}$ values*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Ni | 0 | 0 | 0 | 2·39 (2) |
| N(1) | 0·3084 (1) | 0·1430 (1) | −0·4766 (6) | 5·1 (1) |
| N(2) | 0·0888 (1) | 0·0871 (1) | −0·1268 (4) | 2·6 (1) |
| C(1) | 0·2488 (1) | 0·1003 (1) | −0·3706 (5) | 3·5 (1) |
| C(2) | 0·1719 (1) | 0·0470 (1) | −0·2474 (5) | 2·8 (1) |
| C(3) | 0·0794 (1) | 0·1794 (1) | −0·1146 (5) | 3·1 (1) |
| C(4) | 0 | 0·2241 (1) | 0 | 3·3 (1) |

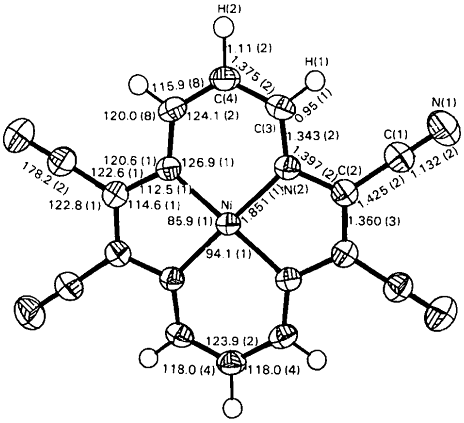

Fig. 1. The molecular structure, labeling scheme, and interatomic distances (Å) and angles (°).

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* Tables of anisotropic temperature factors, positional parameters of H atoms and structure factors, and an *ORTEP* (Johnson, 1965) drawing of the contents of the unit cell have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42105 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of corresponding bond distances* (Å) *and angles* (°) *in* [Ni($C_{14}H_6N_8$)], [Ni(disn)$_2$], [Ni($C_{18}H_{14}N_4$)] *and free damn*

| | [Ni($C_{14}H_6N_8$)] | [Ni(disn)$_2$] | [Ni($C_{18}H_{14}N_4$)] | damn |
|---|---|---|---|---|
| Ni–N(2) | 1·851 (1) | 1·827 (3) | 1·870 (2) | |
| C(2)–C(2′) | 1·360 (3) | 1·403 (5) | 1·399 (3) | 1·363 (6) |
| C(2)–N(2) | 1·397 (2) | 1·331 (4) | 1·418 (3) | 1·392 (8) |
| N(2)–C(3) | 1·343 (2) | | 1·327 (3) | |
| C(3)–C(4) | 1·375 (2) | | 1·384 (4) | |
| C(1)–C(2) | 1·425 (2) | 1·438 (5) | | 1·439 (7) |
| N(1)–C(1) | 1·132 (2) | 1·135 (5) | | 1·165 (10) |
| | | | | |
| N(2)–Ni–N(3) | 94·1 (1) | 95·7 (1) | 94·8 (1) | |
| N(2)–C(2)–C(1) | 122·6 (1) | 124·4 (3) | 126·6 (2) | 117·6 (3) |
| N(2)–C(2)–C(2′) | 114·6 (1) | 113·2 (3) | 113·6 (2) | 124·1 (4) |
| C(1)–C(2)–C(2′) | 122·8 (1) | 122·4 (3) | 119·9 (2) | 118·1 (8) |
| C(2)–N(2)–C(3) | 120·6 (1) | | 120·2 (2) | |
| Ni–N(2)–C(3) | 126·9 (1) | | 125·9 (2) | |
| Ni–N(2)–C(2) | 112·5 (1) | 114·6 (2) | 113·9 (2) | |
| C(4)–C(3)–N(2) | 124·1 (2) | | 124·7 (2) | |
| C(3)–C(4)–C(3′) | 123·9 (2) | | 124·1 (2) | |
| C(2)–C(1)–N(1) | 178·2 (2) | 177·8 (4) | | 179·8 (9) |
| | | | | |
| Reference | This work | Peng *et al.* (1984) | Weiss *et al.* (1977) | Penfold & Lipscomb (1961) |

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# Structure of Triaqua(D,L-β,β-dimethylcysteato)copper(II) Dihydrate, [Cu($C_5H_9NO_5S$)($H_2O$)$_3$].2$H_2O$

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**Abstract.** $M_r$ = 348·81, monoclinic *Cc*, $a$ = 13·605 (2), $b$ = 11·163 (1), $c$ = 9·560 (2) Å, $\beta$ = 117·07 (2)°, $U$ = 1292·9 (7) Å$^3$, $Z$ = 4, $D_m$ = 1·785 (5), $D_x$ = 1·792 Mg m$^{-3}$, $\mu$(Mo $K\alpha$, $\lambda$ = 0·71073 Å) = 1·89 mm$^{-1}$, $F(000)$ = 724, $T$ = 297 (1) K, $R_F$ = 0·023 for 1164 reflections. The structure contains $Cu^{II}$ ions linked by *syn-anti* carboxylate bridges to form zigzag –(Cu—O—C—O)– chains parallel to **c**. Each $Cu^{II}$ ion is tetragonally coordinated. Equatorial $NO_3$ ligation is provided by the two carboxylate O atoms [1·949 (3) and 1·957 (3) Å] and the amino N atom [1·986 (3) Å] of the tridentate β,β-dimethylcysteate ligand, and one water molecule [1·983 (3) Å]. Two additional water molecules form weak axial bonds with Cu [2·471 (3) and 2·572 (5) Å] and complete the $NO_5$ coordination.

**Introduction.** We have been interested in copper complexes of penicillamine and related ligands because of their possible relevance to the chemotherapeutic treatment of Wilson's disease (Birker & Freeman, 1977) as well as their potential usefulness as electronic–structural models for the chromophores present in the blue copper proteins (Schugar, 1983). As part of these studies, a dimeric disulfide complex {bis[copper(II)–D-penicillamine disulfide].9$H_2O$ (Thich, Mastropaolo, Potenza & Schugar, 1974)} with an unusual copper–disulfide interaction, and a novel mixed-valence copper mercaptide cluster complex (Schugar, Ou, Thich, Potenza, Felthouse, Haddad, Hendrickson, Furey & Lalancette, 1980) have been prepared and characterized structurally. We report here the structure of the title compound, a copper(II) complex of the oxidized sulfonic acid derivative of D,L-penicillamine. Space-group and cell-dimension data for several related copper(II) complexes containing this ligand were reported by Crowfoot, Bunn, Rogers-Low & Turner-Jones (1949) in their classic X-ray investigation of the structure of penicillin.

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