

Measurements between room temperature and 400 K show that the observed paramagnetism increases with temperature. A logarithmic plot of IT versus $1/T$, where I is the EPR intensity as measured by the product of the square of the line width and the peak height and T the absolute temperature, gives a linear dependence. From the slope an activation energy J for the paramagnetism of about 0.15 eV can be calculated from $IT \sim \exp(-J/kT)$. Compared with the activation energy of 0.25 eV found for the TCNQ dimers in $[\text{Pt}(\text{dipy})_2][\text{TCNQ}]_2$, the relatively small value of 0.15 reflects the fact that no strong bond exists between the TCNQ anions in the present case, in contrast to the diamagnetic $[\text{Pt}(\text{dipy})_2][\text{TCNQ}]_2$.

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Comparison of an OD and an Ordered Structure of Nickel and Copper Malondiamidine Complexes

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Bis(malondiamidine)nickel(II) dichloride, $[\text{Ni}(\text{C}_3\text{H}_8\text{N}_4)_2]\text{Cl}_2$, forms an OD structure. The stacking of orthorhombic layers of molecules results in a monoclinic structure with $a_m = b_m = 16.37$ (1), $c = 5.121$ (3) Å, $\gamma_m = 109.93$ (4)°, space group $B2/b$. Frequent stacking faults lead to domains in twinned positions, twin law $(110)_m$. The corresponding observed diffuse scattering is qualitatively explained with a range of interaction extending to next-nearest neighbours. The structure has been refined to $R = 8.1\%$ (4.8% for the sharp reflections). The ordered structure of bis(malondiamidine)copper(II) diperchlorate $[\text{Cu}(\text{C}_3\text{H}_8\text{N}_4)_2](\text{ClO}_4)_2$ has been solved at 200 K and refined to $R = 3.6\%$. It is monoclinic with $a = 10.727$ (4), $b = 9.719$ (3), $c = 7.739$ (2) Å, $\beta = 92.12$ (2)°, space group $I2/m$. The two structures are very similar. The six-membered chelate rings are in the boat form with metal–NH–C(NH₂)–C planar. Ni–N is 1.87 (1), Cu–N 1.956 (1) Å. Comparisons are made with similar complexes and the free ligand.

Introduction

The structures of neutral, mono- and diprotonated biguanide, $\text{C}_2\text{H}_7\text{N}_5$, (Pinkerton & Schwarzenbach, 1977; Ernst & Cagle, 1977; Ernst, 1977) and of the

square-planar complex of biguanide with Ni^{II} (Creitz, Gsell & Wampler, 1969) show that in each case the π electrons are delocalized over the whole molecule. The protonated forms are not planar, because of steric hindrance, but all atoms have approximate trigonal

Table 1. *Crystal data and structure determination*

	(I) OD structure	(II) Ordered structure
Formula	[Ni(C ₃ H ₈ N ₄) ₂]Cl ₂	[Cu(C ₃ H ₈ N ₄) ₂](ClO ₄) ₂
Colour	Yellow	Red
Space group	Monoclinic, <i>B2/b</i>	Monoclinic, <i>I2/m</i>
Temperature (K)	293	200
Lattice constants (Å, °)	$a_m = b_m = 16.37$ (1), $c = 5.121$ (3), $\gamma_m = 109.93$ (4)	$a = 10.727$ (4), $b = 9.719$ (3) $c = 7.739$ (2), $\beta = 92.12$ (2)
<i>Z</i>	4	2
Density (floatation) (g cm ⁻³)	$D_o = 1.67$, $D_c = 1.70$	$D_o = 1.87$, $D_c = 1.91$
Point symmetry of complex	1, constrained to <i>2/m</i>	<i>2/m</i>
μ (cm ⁻¹)	19.0	18.0
Crystal dimensions (mm)	0.2	0.11 to 0.30
Absorption correction	None	Between 1.182 and 1.268
Largest $\sin\theta/\lambda$ (Å ⁻¹)	0.5959	0.8586
<i>R</i> for equivalent intensities	2 octants measured, 0.022	2 quadrants to $\sin\theta/\lambda = 0.7$, 0.016
Number of independent reflections	Sharp 355, diffuse 502	2064
Number of parameters	45	83
<i>R</i>	Overall 0.081, sharp 0.048 diffuse 0.144	0.036

symmetry indicating *sp*² hybridization. In the metal complex, the six-membered chelate rings are planar, and the proton of the central imino group is easily lost in alkaline solution (pH ~12). This group is important for the stability of the biguanide complexes. By replacing it by a C atom, malondiamidine, C₃H₈N₄, is obtained where the π bonds extend over only half the molecule, the central methylene group being tetrahedral with C—C lengths of 1.499 Å in the diprotonated cation (Pinkerton & Schwarzenbach, 1977). Its complexes with Ni^{II} and Cu^{II} are much less stable than those of biguanide. Addition of acid or alkali to their aqueous solutions destroys them rapidly. They even decompose slowly in neutral solution so that they are not easily recrystallized. Crystals of the Cu complex are red and their aqueous solution is purple. The corresponding Ni complex is deep yellow. Their preparation and chemistry are described by Schwarzenbach & Schwarzenbach (1977).

The chlorides of the Ni and Cu complexes form well shaped crystals. Their nearly identical diffraction photographs show rather large orthorhombic unit cells, unusual extinction rules and faint diffuse streaks along reciprocal lattice lines parallel to **b**^{*}, indicating an OD structure (one-dimensional disorder). Large crystals of the fluorides were prepared, but their diffraction images resembled powder diagrams. Finally, satisfactory crystals of bis(malondiamidine)copper perchlorate were obtained, whereas the analogous Ni salt could not be recrystallized.

An OD structure may occur if the symmetry of a single layer is higher than the symmetry of a stack of layers (Dornberger-Schiff, 1966). This symmetry information should greatly facilitate the solution of the structure. In order to judge the results obtainable from an OD structure, and to study the exact geometry of

the complexes and their packing, we have solved the disordered structure of bis(malondiamidine)nickel dichloride at room temperature, and the ordered structure of bis(malondiamidine)copper diperchlorate at 200 K.

Experimental and structure-determination parameters

Table 1 shows the important experimental parameters. All measurements were carried out on a Syntex *P2*₁ diffractometer with Nb-filtered Mo *K* α radiation ($\lambda = 0.70926$ Å). The low-temperature data were obtained with the Syntex LTI equipment whose stability was not better than $\pm 5^\circ$. The lattice constants were refined from reflections at 2θ about 40° with symmetry constraints. The crystal form of (II) (Table 1) was measured to an accuracy of 0.002 mm with an optical telescope attached to the 2θ arm of the diffractometer. Backgrounds were determined by profile analysis based on the minimal σ/I criterion (Schwarzenbach, 1977). The standard deviations of the

Table 2. *Atomic coordinates of bis(malondiamidine)-nickel(II) dichloride, OD structure*

The complex is constrained to point symmetry *2/m*.

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	0.25	0.0	0.25
N(11)	0.2422 (4)	0.0919 (7)	0.453 (1)
N(12)	0.3419	-0.0078	0.453
N(21)	0.2855 (4)	0.2045 (7)	0.769 (3)
N(22)	0.4545	0.0355	0.769
C(2)	0.3937 (4)	0.1437	0.618 (2)
C(11)	0.3000 (6)	0.147 (1)	0.607 (2)
C(12)	0.397	0.0500	0.607
Cl	0.4215 (1)	0.3285	0.1745 (4)

Table 3. Atomic coordinates of bis(malondiamidine)-copper(II) diperchlorate, ordered structure

	x	y	z
Cu	0.0	0.0	0.0
N(11)	-0.0400 (1)	0.1415 (1)	0.1689 (2)
N(21)	-0.1383 (1)	0.2309 (2)	0.4076 (2)
C(2)	-0.1865 (2)	0.0	0.3185 (4)
C(11)	-0.1140 (1)	0.1312 (1)	0.2956 (2)
Cl	0.36703 (5)	0.0	0.24850 (7)
O(1)	0.3435 (1)	0.1212 (1)	0.3480 (2)
O(2)	0.4958 (2)	0.0	0.2011 (2)
O(3)	0.2894 (2)	0.0	0.0949 (3)
H(1)	-0.256 (3)	0.0	0.222 (4)
H(2)	-0.219 (3)	0.0	0.432 (4)
H(3)	-0.009 (2)	0.207 (2)	0.164 (2)
H(4)	-0.186 (2)	0.219 (2)	0.483 (3)
H(5)	-0.110 (2)	0.298 (2)	0.397 (2)

intensities were computed from counting statistics and the variation of periodically measured check reflections, and used for weighting in the least-squares refinement.

The weak diffuse reflections of the OD structure were measured in the same way as the sharp reflections (see below). Scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965), dispersion factors for Ni, Cu and Cl from Cromer & Liberman (1970). Calculations were performed with a CDC version of XRAY system (1972), modified where necessary. Final atomic coordinates are given in Tables 2 and 3.†

Solution of the OD structure

Precession photographs of bis(malondiamidine)-nickel(II) dichloride indicated an orthorhombic unit cell with $a_o = 18.79$ (2), $b_o = 26.80$ (3), $c_o = 5.121$ (3) Å, where only the following reflections were observed (Fig. 1): h_o, k_o even, $\frac{1}{2}(h_o + k_o) + l$ even (sharp reflections); h_o, k_o odd, $l \neq 0$ (diffuse reflections sitting on faint streaks parallel to \mathbf{b}_o^*).

These extinction rules can be explained by the superposition of two monoclinic lattices with $\mathbf{a}_m^* = \mathbf{b}_m^* = \mathbf{a}_o^* - \mathbf{b}_o^*$, $\mathbf{b}_m^* = \mathbf{a}_m^* = \mathbf{a}_o^* + \mathbf{b}_o^*$, $a_m = b_m = 16.37$ (1) Å, $\gamma_m = 109.93$ (4)°, and with extinction rules of the space groups $B2/b$ or Bb (first setting): $h_m k_m l$: $h_m + l$ even; $h_m k_m 0$: h_m, k_m both even. The reflection $h_m k_m l$ of one lattice coincides with $k_m h_m \bar{l}$ of the other. The sharp

† Lists of structure factors and anisotropic thermal parameters for both structures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33304 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

reflections ($h_m + k_m$ even, $k_m + l$ even) are thus common to both orientations, whereas the diffuse intensities ($k_m + l$ odd) do not superimpose, $k_m h_m l$ being extinct due to the B centring. The streaks of diffuse intensity indicate a stacking disorder of orthorhombic layers perpendicular to \mathbf{b}_o , rather than macroscopic twinning.

The sharp reflections define an orthorhombic subcell with $\mathbf{a}'_o = \frac{1}{2}\mathbf{b}_o$ and $\mathbf{b}'_o = \frac{1}{2}\mathbf{b}_o$, containing two formula units, and with space-group symmetry $Immm$, $Imm2$ or $I222$. The highest point symmetry of the complex is $2/m$. This would be mmm for planar chelate rings. If four such highly symmetric planar molecules were placed in the monoclinic cell with their mirror planes parallel to $(001)_m$, $(110)_m$ and $(\bar{1}10)_m$ and with the Ni atoms at $\frac{1}{4}, 0, \frac{1}{4}$, the space-group symmetries $B2/b$ or Bb would in fact reduce to $Immm$. The sharp reflections alone define a symmetrized superposition structure of the real structure composed of non-planar molecules. If their mirror planes are parallel to $(\bar{1}10)_m$, $B2/b$ leads to $Immm$, Bb to $I2mm$. No deviation from centrosymmetry could be detected during structure determination, and $B2/b$ has therefore been accepted.

The disorder arises because layers of molecules parallel to orthorhombic $(010)_o = (\bar{1}10)_m$ retain orthorhombic symmetry. For $l = 0$, intensities $h_o k_o 0$ are observed only for h_o even, indicating a glide-reflection line parallel to \mathbf{a}_o . The symmetry of a layer is therefore $mP2mg$ (Niggli, 1964), the first symbol indicating a mirror plane parallel to the centrosymmetric layer. The molecular symmetry is then $2/m$. Reciprocal lattice

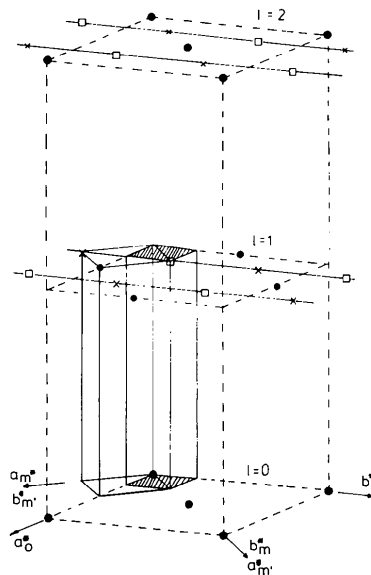


Fig. 1. Reciprocal lattice of the OD structure with orthorhombic ($\mathbf{a}_o^*, \mathbf{b}_o^*$) and monoclinic ($\mathbf{a}_m^*, \mathbf{b}_m^*$; $\mathbf{a}_m^*, \mathbf{b}_m^*$) cells. ● main reflections, h_o and k_o even, $\frac{1}{2}(h_o + k_o) + l$ even; $h_m + k_m$ and $k_m + l$ even. ● and × belong to the monoclinic lattice $\mathbf{a}_m^*, \mathbf{b}_m^*, c$. ● and □ belong to the monoclinic lattice $\mathbf{a}_m^*, \mathbf{b}_m^*, -c$.

rows (h_o, l_o) with only sharp reflections, *i.e.* h_o even, are structure seminvariants with respect to the stacking positions. They are explained if adjacent layers are displaced by $\pm \frac{1}{4}\mathbf{a}_o + \frac{1}{2}\mathbf{b}_o + \frac{1}{2}\mathbf{c}_o$, which leads to two possible stacking positions equivalent with respect to nearest neighbours and displaced by $\frac{1}{2}\mathbf{a}_o$ (Fig. 2). There are four possible layer positions A, B, C and D in the orthorhombic cell, with $B = A + (-\frac{1}{4}\mathbf{a}_o + \frac{1}{2}\mathbf{c}_o)$, $C = A + (\frac{1}{4}\mathbf{a}_o, 0)$ and $D = A + (\frac{1}{4}, \frac{1}{2})$. A and C are followed by B or D , and B and D by A or C . A stack with different next-nearest neighbours, *e.g.* ABC , may be denoted by M and a stack with identical next-nearest neighbours, *e.g.* ABA , by O . Any stacking sequence is then represented by a succession of M and O , in analogy to the Jagodzinski (1949) symbols for close sphere packings. The limiting structures with highest order (Dornberger-Schiff, 1966) are: (a) $\dots MMM\dots$, symmetry $B2/b$. A stacking fault $\dots MMMOMMM\dots$ leads to a twin position. For h_o odd, k_o must be odd, as observed. (b) $\dots OOO\dots$, symmetry $Pnma$. A stacking fault $\dots OOOMOOO\dots$ leads to a parallel displacement. For h_o odd, k_o must be even, contrary to observation.

Symmetry considerations lead therefore to the monoclinic structure with frequent stacking faults. This is confirmed by a more detailed calculation of the diffuse streaks (Jagodzinski, 1949; Mering, 1949; Schwarzenbach, 1969). Let $P_{rs}^{(m)}$ be the probability that a layer with position s is found m layers distant from one with position r . Clearly,

$$P_{AB}^{(2n)} = P_{AD}^{(2n)} = P_{AC}^{(2n+1)} = P_{AA}^{(2n+1)} = 0.$$

Since all positions are, in the mean, equivalent, $P_{AB}^{(m)} = P_{BC}^{(m)} = \dots$ *etc.* The average symmetry of the crystal is orthorhombic, therefore

$$P_{AB}^{(2n+1)} = P_{AB}^{-(2n+1)} = P_{BA}^{(2n+1)} = P_{AD}^{(2n+1)} = \frac{1}{2},$$

i.e. the two orientations of an M stack occur with equal probability. We need thus only consider the probabilities $P_{AC}^{(2n)}$ and $P_{AA}^{(2n)} = 1 - P_{AC}^{(2n)}$. The intensity

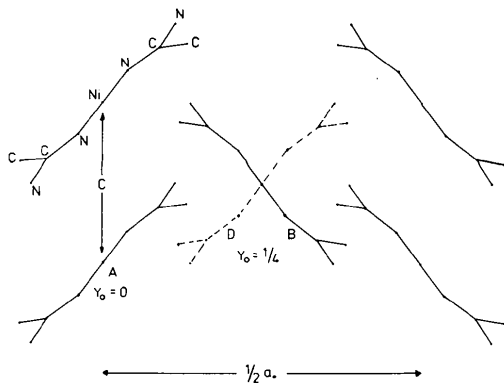


Fig. 2. Schematic diagram of the OD structure projected along orthorhombic \mathbf{b}_o . B and D are alternative positions of a layer stacked on layer A .

parallel to \mathbf{b}_o^* is therefore proportional to the squared structure amplitude

$$G = \sum_{m=-(N-1)}^{N-1} (N - |m|) \sum_s P_{As}^{(m)} F_A F_s^* \exp\left(-\frac{\pi}{2} i k_o m\right)$$

where N is the number of layers, F_A and F_s are the structure factors of layers A and s , referred to an origin within the layer, which differ only in phase because of their displacement along \mathbf{a}_o and \mathbf{c}_o , and k_o refers to the \mathbf{b}_o vector which spans four layers. F_A and F_s are only non-zero for integral h_o and l . With $|F|^2 = |F_A|^2$ and $J(k_o) = \sin^2(N\pi k_o)/\sin^2(\pi k_o)$, we obtain for h_o and k_o even, $\frac{1}{2}(h_o + k_o) + l$ even: $G = |F|^2 J(k_o)$, sharp reflections; for h_o odd:

$$G = |F|^2 \left\{ N + 2 \sum_{n=1}^{\frac{1}{2}N} (N - 2n) [1 - 2P_{AC}^{(2n)}] \cos \pi k_o n \right\}$$

$$\simeq N |F|^2 \left\{ 1 + 2 \sum_1^{\infty} [1 - 2P_{AC}^{(2n)}] \cos \pi k_o n \right\};$$

in all other cases $G = 0$. For the ordered structures, this reduces to

$$G(h_o \text{ odd}) = \frac{1}{2} |F|^2 J(k_o),$$

k_o being odd for M , and even for O .

The ordered M structure consists then of macroscopic twins of equal volume. With a range of interaction between layers reaching next-nearest neighbours, the probabilities are completely defined by $W = P_{AC}^{(2)}$, the probability of finding an M stack. We then obtain the recursion formula

$$P_{AC}^{(2n)} = W P_{AA}^{(2n-2)} + (1 - W) P_{AC}^{(2n-2)};$$

therefore

$$P_{AC}^{(2n)} = \frac{1}{2} [1 - (1 - 2W)^n],$$

and

$$G(h_o \text{ odd}) = N |F|^2 \frac{W(1 - W)}{W^2 + (1 - 2W) \sin^2 \frac{1}{2} \pi k_o}$$

$$= N |F|^2 I(W).$$

For $W > \frac{1}{2}$, the interference function $I(W)$ has maxima at k_o odd and minima at k_o even, *i.e.* we obtain the disordered twin structure. For $W < \frac{1}{2}$, the maxima and minima are reversed. For $W = \frac{1}{2}$, the layers scatter independently, the range of interaction being limited to next-nearest neighbours. A larger range of interaction would be described by the probabilities of finding M following M , and O following O . Maxima at all integer k_o values would generally be found (Schwarzenbach, 1969). We need thus only postulate an interaction between next-nearest layers favouring the M structure.

The intensities of the sharp reflections do not depend on the stacking sequence. Thus, strictly orthorhombic layers in a monoclinic single crystal lead to the same intensities for $h_m k_m l$ and $k_m h_m l$ ($h_m + k_m$ even), so that then the twin model does not superimpose inequivalent

reflections. On the other hand, only half the crystal volume contributes to a diffuse reflection, since it originates from domains of only one orientation; the reflection $k_m h_m l$ from domains in the twinned position is space-group extinct. Since $I(W)$ is observed with reasonably sharp maxima, we assume that the integrated intensities of the diffuse reflections are roughly proportional to $|F|^2$ at integral k_o values, thus implying that $I(W)$ varies much faster than $|F|^2$. They have to be scaled, however, by a factor corresponding to the integral of $I(W)$ over the scan interval which is not strictly constant. As an approximation, they were assigned a scale factor which was allowed to vary independently during refinement, rather than an intensity scale of 0.5 corresponding to macroscopic twinning. Its deviation from 0.5 is a measure of the crystal volume occupied by approximately perfect domains.

The superposition structure with symmetry $Immm$ was easily solved, the Ni atoms occupying positions 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The two superimposed images of the complex were anisotropically refined to $R = 0.041$ with a goodness of fit of 4.7. The diffuse reflections were used to desymmetrize the structure, *i.e.* to locate unambiguously the Cl⁻ ions, and to resolve the nearly superimposed N(21) and N(22). The structure was anisotropically refined in $B2/b$. To preserve exact orthorhombic layer symmetry, additional constraints were introduced. For the different sites, we obtain: (a) Ni in $2/m$: $x, y, z = \frac{1}{4}, 0, \frac{1}{4}$; $U_{11} = U_{22}$, $U_{13} = U_{23}$; (b) C(2) in m : $x - y = \frac{1}{4}$; $U_{11} = U_{22}$, $U_{13} = U_{23}$; (c) local symmetry links two independent positions for N(11) and N(12), N(21) and N(22), C(11) and C(12): $x(1) - y(2) = x(2) - y(1) = \frac{1}{4}$, $z(1) = z(2)$, $U_{11}(1) = U_{22}(2)$, $U_{22}(1) = U_{11}(2)$, $U_{33}(1) = U_{33}(2)$, $U_{12}(1) = U_{12}(2)$, $U_{13}(1) = U_{23}(2)$, $U_{23}(1) = U_{13}(2)$; (d) local symmetry imposed on a single position for Cl: $x + y = \frac{3}{4}$, $U_{11} = U_{22}$, $U_{13} = -U_{23}$.

Together with the second scale factor, this leads to an increase of five parameters over the superposition structure. H atoms were not considered. The refinement converged to $R = 0.081$, the sharp reflections alone giving 0.048, the diffuse reflections 0.144. The goodness of fit is 4.4 with similar contributions from both reflection groups. Bond lengths and angles are, with the exception of C(11)–C(2), within 2σ of those of the superposition structure, and the temperature factors show the same characteristic.

The two scale factors and their e.s.d.'s, defined by $F_o \times \text{scale} \simeq F_c$, are 0.966 (0.004) for the sharp reflections and 1.723 (0.019) for the diffuse. The square of their ratio is 0.314 (0.008), the expected value for a macroscopic twin being 0.5.

Refinement of a macroscopic twin model, again with two scale factors, allowing the layer symmetry to deviate from orthorhombic and treating the sharp reflections as superpositions of two inequivalent intensities did not result in an improvement.

Solution of the ordered structure

The ordered structure of bis(malondiamidine)copper(II) diperchlorate was solved by Patterson and Fourier techniques. It was refined anisotropically, with isotropic H atoms to $R = 0.036$. Isotropic extinction (Zachariassen, 1967) proved to be negligible. A final difference synthesis showed electron density on most of the bonds, but electron density studies were abandoned since the temperature was not constant enough during measurement.

Discussion

Fig. 3 shows distances and angles. Both complexes have $2/m$ symmetry. The metal atoms are four-coordinate with a square-planar configuration. No additional atoms are near enough to be coordinated. The six-membered chelate rings are in the boat form. π bonding extends over N(11), C(11) and N(21) which form, together with C(2), H(3), H(4), H(5) and the metal atom, a nearly perfect plane. Maximum deviations from the least-squares plane through the metal atom, N(11), C(11), N(21) and C(2) are 0.06 Å for the Ni complex, 0.016 Å for the Cu complex and 0.046 Å for the H atoms in the latter. The two plane normals of the boat make an angle of 40.1 (Ni) and 39.83° (Cu). Taking into account the low accuracy of the OD structure, the dimensions of the malondiamidine ligands agree well, except for C(11)–C(2). This could indicate an inadequate model for the OD structure. The corresponding temperature factor of C(2) is also suspect with $U = 0.009 \text{ \AA}^2$ perpendicular to the mirror plane, 0.023 and 0.052 Å² in the mirror

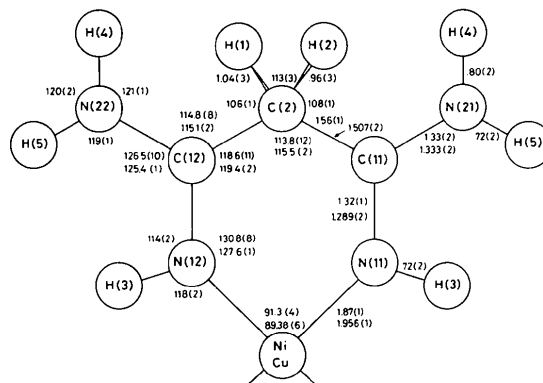


Fig. 3. Distances and angles in the malondiamidine complexes. Upper numbers refer to the Ni complex (OD), lower numbers and the hydrogen bond lengths and angles to the Cu complex (ordered structure). The symmetry of the molecule is $2/m$, *i.e.* N(11) and N(12), C(11) and C(12), N(21) and N(22) are equivalent by the layer symmetry (Ni) or space-group symmetry (Cu).

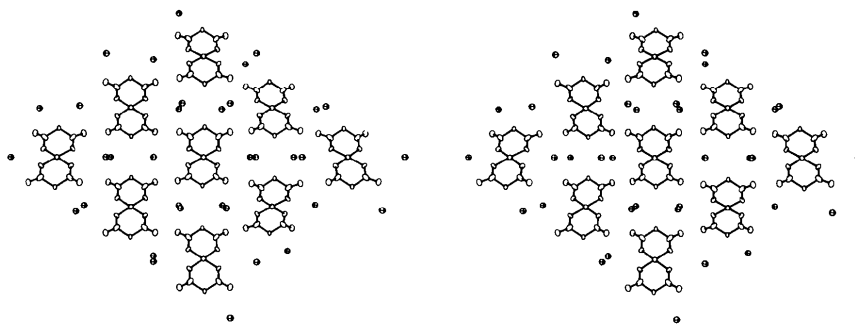


Fig. 4. View of the (001) plane of the monoclinic OD structure of bis(malondiamidine)nickel(II) dichloride. $\mathbf{b}_o = -\mathbf{a}_m + \mathbf{b}_m$ points from left to right. The stacking sequence along \mathbf{b}_o is *ABCD*A.

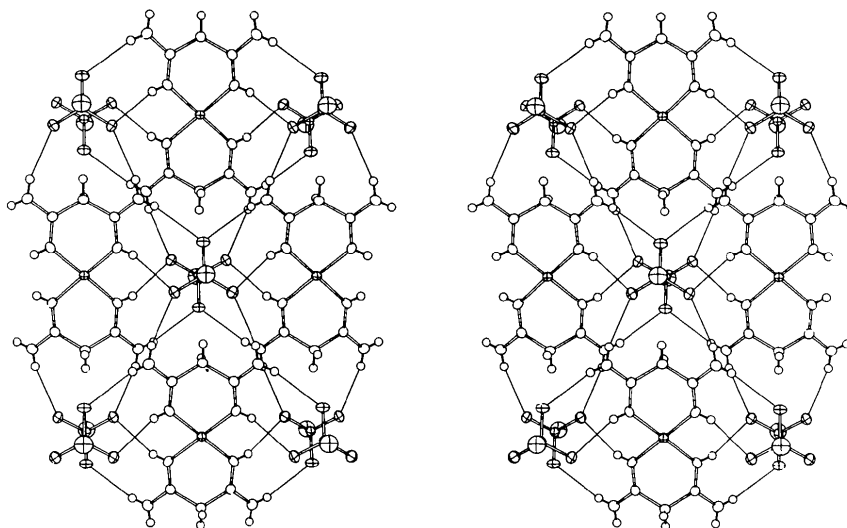


Fig. 5. View of the (101) plane of the structure of bis(malondiamidine)copper(II) diperchlorate. \mathbf{b} points from left to right, $\mathbf{a} - \mathbf{c}$ from top to bottom. The O atom of the perchlorate ion sticking out of the hydrogen-bonded layer [O(3)] has a close contact with a methylene H atom of the next layer.

plane. The distance is somewhat smaller in the orthorhombic superposition structure (1.53 Å), but the temperature factor shows the same anomaly as before. The macroscopic twin model gives 1.54 Å. The C—C distances in two complexes of Mn with malonic acid (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977) vary between 1.550 (13) and 1.482 (7) Å. The free protonated ligand in malondiamidinium sulphate (Pinkerton & Schwarzenbach, 1977) also consists of two planar parts with two equal C—C distances of 1.499 (4) and four nearly equal N—C distances of 1.304 (4) Å.

In the metal complexes, the N—C distances become slightly unequal, as in the more stable Ni biguanide complex (Creitz, Gsell & Wampler, 1969). The relative instability of the malondiamidine complex in aqueous solution could be due to the more symmetrical free ligand. Biguanide on the other hand is planar in the

complex, but the free biguanidinium ion is severely twisted out of plane by the steric hindrance of the H atoms which weakens the π -bonding resonance.

Published bond lengths between Ni^{II} and imino N range from 1.86 to 1.89 Å. Data for the six-membered chelate ring in [*N,N'*-di(2-aminoethyl)malondiamidato]nickel(II) trihydrate (Lewis, Nancollas & Coppens, 1972) are very similar to ours with Ni—N = 1.869 Å. In the Ni biguanide complex, 1.87 Å is found, and in ethylenebis(biguanidine)nickel(II) dichloride monohydrate (Holian & Marsh, 1970), the mean bond length is 1.865 Å. The mean Cu—N distance in the analogous ethylenebis(biguanidine)copper(II) dichloride (Mathew & Kunchur, 1970) is 1.963 Å, again in good agreement with our results.

Packing diagrams of the two structures are shown in Figs. 2, 4 and 5. In the OD structure, the molecules are stacked along \mathbf{c} , the stacks forming layers which are

held together by the Cl^- ions. The structure determination shows that the range of interaction extends only to next-nearest neighbours. The more bulky ClO_4^- ions in the ordered structure lead to an entirely different hydrogen-bonded structure. O(11) and O(2) both accept two hydrogen bonds each, with $\text{O}\cdots\text{H}-\text{N}$ angles between 161 and 166° , whereas O(3) has a close contact of 2.46 \AA with H(1), the angle $\text{C}(2)-\text{H}(1)\cdots\text{O}(3)$ being 142° .

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The Crystal and Molecular Structure of Tetrachloroqua[2,4,6-tris(2'-pyridyl)-1,3,5-triazine]dicobalt(II) Monohydrate

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$[\text{C}_{18}\text{H}_{12}\text{N}_6(\text{H}_2\text{O})\text{Co}_2\text{Cl}_4] \cdot \text{H}_2\text{O}$ is monoclinic, space group $P2_1/a$, with $a = 26.77(7)$, $b = 10.88(3)$, $c = 8.63(2) \text{ \AA}$, $\beta = 99.2(2)^\circ$, $Z = 4$. The structure was refined to $R = 0.108$ for 708 visually estimated reflexions. The ligand functions primarily as tridentate and monodentate to the two Co atoms. Co(1) is at the centre of a distorted octahedron of two Cl atoms [Co–Cl $2.23(1)$, $2.55(1) \text{ \AA}$], one water molecule [Co–O $2.19(3) \text{ \AA}$] and three N atoms of the ligand [mean Co–N $2.07(3) \text{ \AA}$]. Co(2) is surrounded by three Cl atoms [mean Co–Cl $2.22(1) \text{ \AA}$] and one pyridyl N atom [Co–N $1.99(3) \text{ \AA}$] forming a distorted tetrahedron. A Cl atom bridges Co(1) and Co(2) of adjacent molecules to form molecular chains parallel to [010]. Severe distortions in the ligand molecule are apparent. The uncoordinated water molecule is associated with the coordinated water, two Cl atoms and the s-triazine ring, which shows distortion to a chair conformation.

Introduction

2,4,6-Tris(2'-pyridyl)-1,3,5-triazine (tpt) has been shown to function primarily as a tridentate ligand with a variety of transition-metal salts (Barclay, Vagg & Watton, 1977a). From non-aqueous media dimeric

species of general formula $M_2X_4\text{tpt} \cdot n\text{H}_2\text{O}$ (where $M = \text{Ni}$ or Co ; $X = \text{Cl}$ or Br) have been isolated where the ligand may be acting simultaneously as both tridentate and bidentate (Vagg, Warrener & Watton, 1967, 1969). We have reported the crystal structures of a bivalent Ni complex (Barclay, Vagg & Watton, 1977a)