Acta Cryst. (1978). B**34**, 1823–1827

The 1:3 Radical Salt Bis(2,2′-dipyridyl)platinum(II)–7,7,8,8-Tetracyanoquinodimethane, $[Pt(dipy)_2]^{2+}[TCNQ]_3^{2-}$

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(*Received* 11 *November* 1977; *accepted* 16 *December* 1977)

The title compound is triclinic, space group $P\bar{1}$, with $a = 7{\cdot}979$ (5), $b = 10{\cdot}567$ (6), $c = 17{\cdot}203$ (7) Å, $\alpha = 117{\cdot}13$ (3), $\beta = 97{\cdot}19$ (4), $\gamma = 111{\cdot}28$ (5)°, $Z = 1$. The structure was refined to $R = 0{\cdot}073$ for 1312 counter reflections. It consists of stacks of centrosymmetric TCNQ trimers with interplanar distances of 3·23 within and 3·33 Å between trimers. The $[Pt(dipy)_2]^{2+}$ cations have no remarkable interactions with one another nor with the TCNQ moieties. EPR spectra show interacting spins; the activation energy for the paramagnetism is 0·15 eV.

Introduction

The radical anion salts of TCNQ possess interesting electrical and magnetic properties which can be related to their different structural principles (Herbstein, 1971). Depending on the size and the shape of the counter ions, the TCNQ moieties can form infinite equidistant stacks, or stacks composed of dimers, trimers, tetramers and pentamers. Some of the possible TCNQ arrangements have been discussed by Goldberg, Eisenberg, Miller & Epstein (1976). Of special interest are the infinite equidistant stacks, for they can lead to quasi one-dimensional metals, like tetrathiofulvalenium–TCNQ (Phillips, Kistenmacher, Ferraris & Cowan, 1973). We have been working on a project to combine the properties of these organic metals with those of the one-dimensional transition-metal compounds, like $K_2[Pt(CN)_4]Br_{0\cdot3}.3{\cdot}2H_2O$ (Krogmann, 1969). Outstanding physical properties could be expected in compounds with parallel regular stacks of open-shell organic species and mixed-valence transition-metal complexes. Such systems were unknown until now.* There is one example where the organic component stacks, but the inorganic does not: the adduct of tetrathiotetracene and $Ni(S_2C_2H_2)_2$ (Interrante, Bray, Hart, Kasper, Piacente & Watkins, 1977), and one example of mixed stacks of the metal complex and the organic component, the adduct of TCNQ and bis(3-thioxopropene-1-thiolato)-platinum(II) (Mayerle, 1977).

We reacted the organic acceptor TCNQ with planar or nearly planar Pt^{II} complexes with N-containing ligands. In a previous paper (Vu Dong, Endres, Keller, Moroni & Nöthe, 1977) we reported the structure of one of the products, which was nearly diamagnetic and showed the unusual feature of two TCNQ radicals paired by a σ-bond of 1·65 Å between two C atoms of the methylene groups. Meanwhile, a similar σ-paired dimer has been found in *N*-ethylphenazinium–TCNQ (Morosin, Plastas, Coleman & Stewart, 1978).

Experimental

Reaction of $Pt(dipy)_2Cl_2$ with LiTCNQ yields a green powder (Endres, Keller, Moroni & Nöthe, 1976). By recrystallization from a $DMSO/CH_3OH$ mixture two different products are obtained: the nearly diamagnetic $Pt(dipy)_2[TCNQ]_2$ mentioned above and paramagnetic $Pt(dipy)_2[TCNQ]_3$. The structure and EPR properties of the latter are described here. Weissenberg photographs showed the crystals to be triclinic; lattice parameters were derived from the accurate θ values of 26 reflections centred on a computer-controlled automatic three-circle diffractometer (Siemens), by least squares (Berdesinski & Nuber, 1966). They are summarized in Table 1. Intensity measurements on the Siemens diffractometer up to $2\theta = 70°$ with the five-value method and the θ–2θ scan technique yielded 1312 observed reflections with $I > 2{\cdot}58\sigma(I)$. Intensities were corrected only for Lorentz and polarization factors. Calculations were performed on computers Siemens 301 (Anorganisch-Chemisches Institut, Heidel-

Table 1. *Crystal data*

Formula: $Pt(C_{10}H_{10}N_2)_2.(C_{12}H_4N_4)_3$	$F(000) = 538$
FW 1084·04	$\alpha = 117{\cdot}13$ (3)°
Triclinic $P\bar{1}$	$\beta = 97{\cdot}19$ (4)
$a = 7{\cdot}979$ (5) Å	$\gamma = 111{\cdot}28$ (5)
$b = 10{\cdot}567$ (6)	$Z = 1$
$c = 17{\cdot}203$ (7)	$d_c = 2{\cdot}01$ g cm^{-3}

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* Possible exception: $(perylene)_2M(mnt)_2$, mnt = dianion of 1,2-dicyanoethylene-1,2-dithiol (Alcácer & Maki, 1976).

berg) and IBM 370/168 (Universitätsrechenzentrum Heidelberg) with the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were those of Hanson, Herman, Lea & Skillman (1964). EPR spectra were taken on a Bruker B-ER 418 spectrometer with an NMR gauss meter for field calibration and a DANA 320 D microwave frequency counter.

Structure determination and refinement

Space group $P\bar{1}$ was assumed. The Pt atom was placed at 0,0,0 and Fourier syntheses revealed the positions of all the other atoms except the H atoms, which were ignored. Isotropic refinement gave $R = 0{\cdot}102$; refinement with anisotropic temperature factors for Pt yielded $R = 0{\cdot}091$; anisotropic refinement of all atoms converged to $R = 0{\cdot}073$.*

Table 2. *Final atomic parameters* ($\times 10^3$)

	x	*y*	*z*
Pt	0	0	0
C(1)	798 (3)	191 (2)	−6 (2)
C(2)	705 (3)	281 (3)	28 (1)
C(3)	631 (3)	278 (2)	101 (1)
C(4)	653 (2)	181 (3)	131 (1)
C(5)	763 (2)	95 (3)	96 (1)
C(6)	816 (4)	745 (2)	44 (1)
C(7)	732 (3)	701 (3)	101 (1)
C(8)	658 (3)	807 (3)	170 (2)
C(9)	694 (2)	937 (3)	168 (1)
C(10)	769 (2)	980 (2)	112 (1)
C(11)	684 (2)	518 (2)	494 (1)
C(12)	546 (3)	468 (2)	416 (1)
C(13)	347 (3)	451 (2)	418 (1)
C(14)	216 (2)	407 (2)	341 (1)
C(15)	250 (3)	379 (2)	260 (1)
C(16)	38 (3)	382 (2)	340 (1)
C(17)	617 (2)	816 (2)	450 (1)
C(18)	475 (3)	770 (3)	368 (1)
C(19)	293 (2)	748 (2)	372 (1)
C(20)	264 (3)	788 (2)	455 (1)
C(21)	393 (3)	844 (2)	536 (1)
C(22)	584 (3)	857 (2)	535 (1)
C(23)	730 (2)	910 (2)	616 (1)
C(24)	694 (3)	937 (2)	700 (1)
C(25)	921 (3)	922 (2)	616 (1)
C(26)	105 (3)	699 (3)	293 (1)
C(27)	187 (3)	661 (3)	207 (1)
C(28)	35 (6)	330 (3)	713 (1)
N(1)	829 (2)	103 (2)	28 (1)
N(2)	843 (2)	893 (2)	56 (1)
N(3)	299 (2)	350 (2)	188 (1)
N(4)	883 (3)	365 (3)	343 (1)
N(5)	667 (2)	959 (2)	766 (1)
N(6)	61 (2)	932 (2)	614 (1)
N(7)	202 (2)	629 (2)	133 (1)
N(8)	823 (4)	647 (3)	290 (1)

Description of the structure and discussion

Atomic coordinates are listed in Table 2. Figs. 1 and 2 show projections of the structure along **a** and **b** respectively. The structure consists of chains of centrosymmetric $[TCNQ]_3^{2-}$ trimers with interplanar separations of 3·23 within and 3·33 Å between trimers. The modes of overlap within and between trimers can be seen in Figs. 3 and 4. The TCNQ chains are surrounded by isolated $[Pt(dipy)_2]^{2+}$ cations which

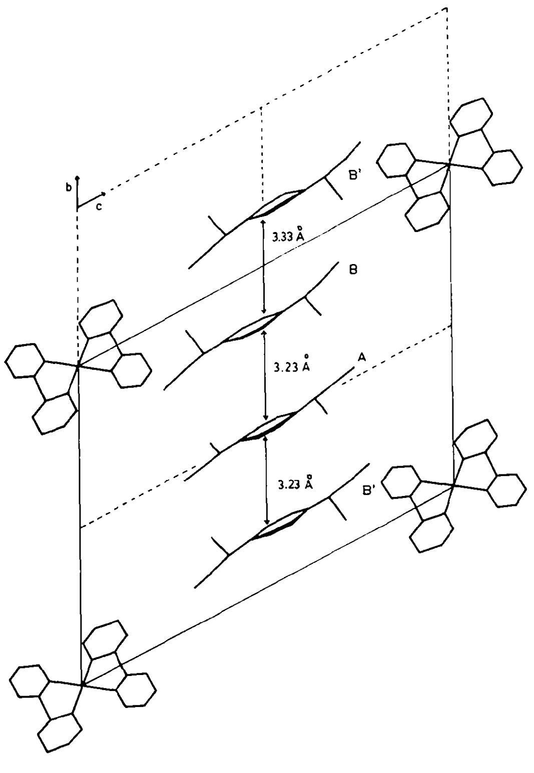

Fig. 1. Projection of the structure on the *bc* plane.

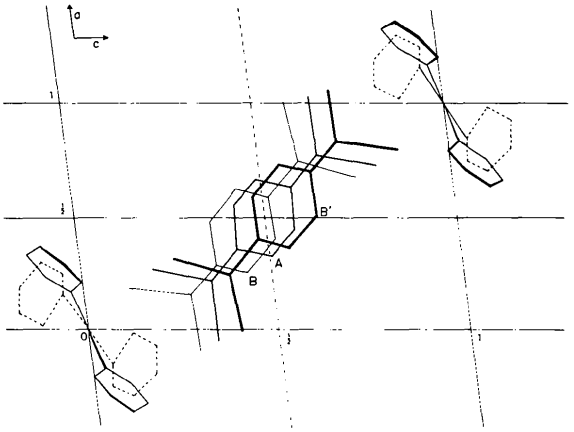

Fig. 2. Projection of the structure on the *ac* plane.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33302 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

have no remarkable interactions with one another or with the TCNQ stacks. Bond distances and angles in the cations are given in Fig. 5. The two halves of one dipy ligand are tilted by 21° with respect to each other, though symmetry requires the four N and the Pt atoms to lie exactly in a plane. A similar geometry of the cation was found for the diamagnetic $[Pt(dipy)_2]^{2+}$-$[TCNQ]_2^{2-}$ (Vu Dong, Endres, Keller, Moroni &

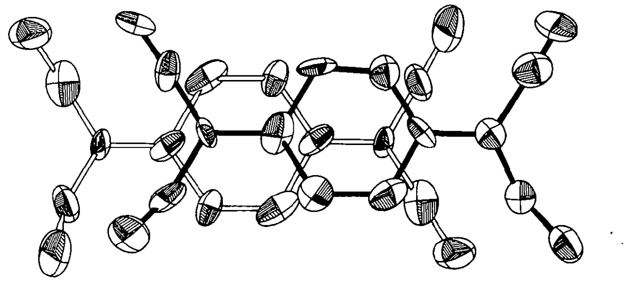

Fig. 3. Projection of two TCNQ molecules within a trimer on each other.

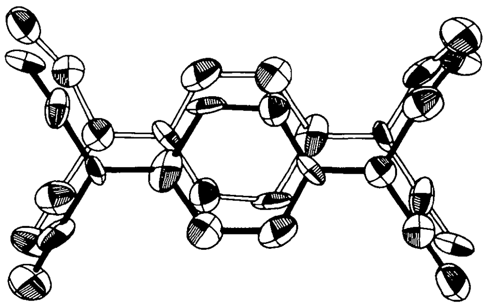

Fig. 4. Projection of two adjacent molecules in different trimers on each other.

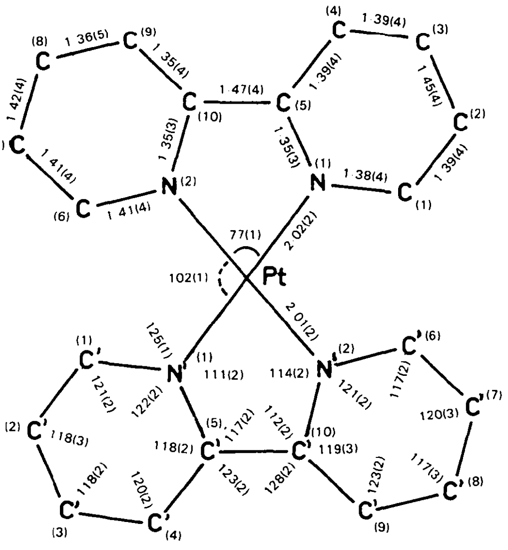

Fig. 5. Bond distances (Å) and angles (°) in the $[Pt(dipy)_2]^{2+}$ cation.

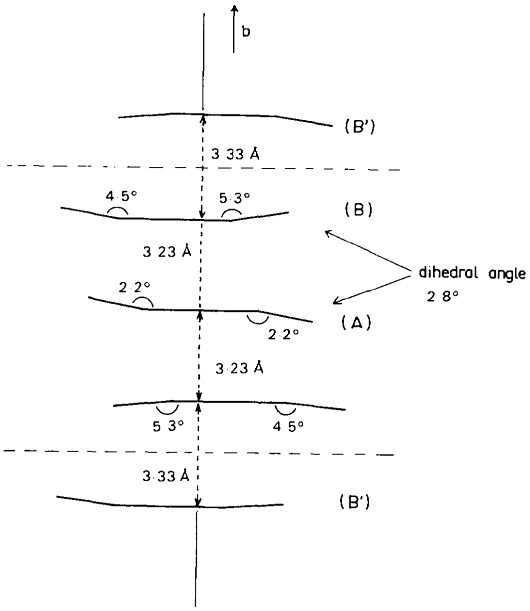

Fig. 6. The general geometry of the $[TCNQ]_3^{2-}$ triads.

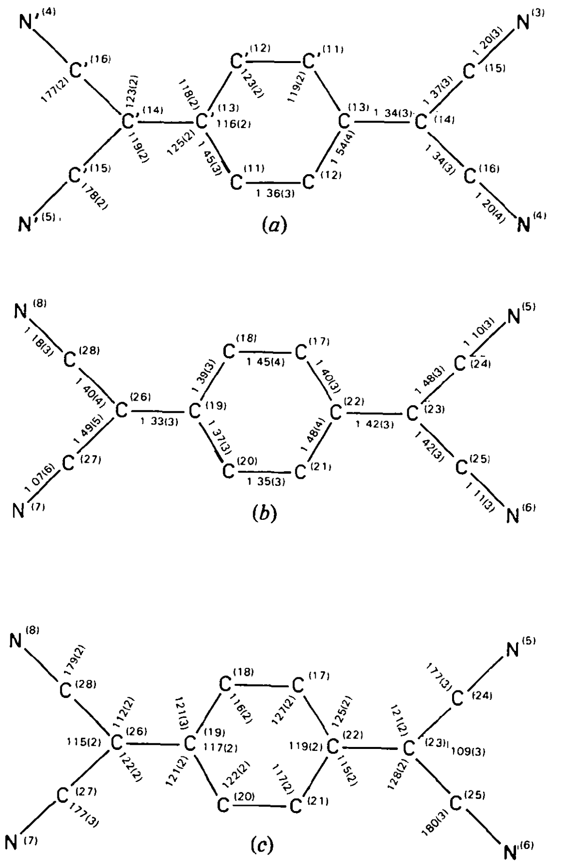

Fig. 7. (a) Bond distances (Å) and angles (°) in the central molecule of a trimer. (b) Bond distances (Å) and (c) angles (°) in the outer molecule of a trimer.

Table 3. *Deviations of the atoms* (Å) *from the best planes through parts of the TCNQ molecules*

The equation of the planes is: $Px + Qy + Rz - S = 0$.

(*a*) TCNQ (*A*) benzenoid ring and methylene C atoms

C(11)	−0·022	C′(11)	0·017
C(12)	−0·016	C′(12)	0·021
C(13)	0·004	C′(13)	−0·002
C(14)	0·006	C′(14)	−0·009

with $P = -0{\cdot}9913$; $Q = 9{\cdot}7649$; $R = -4{\cdot}0512$ and $S = 2{\cdot}3627$

(*b*) TCNQ (*A*) exterior plane

C(14)	−0·014	N(3)	−0·006
C(15)	0·010	N(4)	−0·010
C(16)	0·020		

with $P = -1{\cdot}2783$; $Q = 9{\cdot}8975$; $R = -4{\cdot}1887$ and $S = 2{\cdot}3280$

(*c*) TCNQ (*B*) benzenoid ring

C(17)	−0·028	C(20)	−0·01
C(18)	0·04	C(21)	0·03
C(19)	−0·02	C(22)	−0·01

with $P = -0{\cdot}7874$; $Q = 9{\cdot}8400$; $R = -4{\cdot}7404$ and $S = 5{\cdot}3817$

(*d*) TCNQ (*B*) exterior plane 1

C(23)	−0·0009	N(5)	0·0015
C(24)	−0·0031	N(6)	−0·0037
C(25)	−0·0062		

with $P = -0{\cdot}6410$; $Q = 94801$; $R = 3{\cdot}3623$ and $S = 6{\cdot}0953$

(*e*) TCNQ (*B*) exterior plane 2

C(26)	−0·0478	N(7)	0·0010
C(27)	−0·00001	N(8)	0·0234
C(28)	−0·0721		

with $P = -0{\cdot}1875$; $Q = 0{\cdot}9370$; $R = -0{\cdot}2926$ and $S = 5{\cdot}3885$

Nöthe, 1977). As usual, the TCNQ molecules are not exactly planar. The dihedral angle between the benzenoid rings within a trimer is 2·8°; between adjacent TCNQ molecules of two different trimers it is zero by symmetry. Details are given in Fig. 6. Table 3 shows the equations of relevant planes and the deviations of the atoms. Fig. 7 summarizes the bond distances and angles of the two crystallographically different TCNQ molecules. The standard deviations are rather high [probably caused by crystal quality: the anisotropic temperature factor of C(5) became negative during refinement]. Therefore the usual discussion of the distribution of the negative charges based on bond lengths seems unreasonable.

A detailed discussion of charge distribution and bond lengths together with a discussion of possible stacking modes of TCNQ is given by Goldberg, Eisenberg, Miller & Epstein (1976) in their paper on $[\mathrm{Pd(CNCH_3)_4}][\mathrm{TCNQ}]_4.2\mathrm{CH_3CN}$. $[\mathrm{Pt(dipy)_2}][\mathrm{TCNQ}]_3$ may be compared with [1,4-di(*N*-quinoliniummethyl)benzene]$^{2+}[\mathrm{TCNQ}]_3^{2-}$ (Ashwell, Eley, Wallwork, Willis, Peachey & Wilkos, 1977), in spite of the completely different cations. Chains of $[\mathrm{TCNQ}]_3^{2-}$ trimers with interplanar distances of 3·15 Å within a triad are separated by cations, which also form a sort of chain. There is almost no direct overlap between adjacent triads, whereas such overlap occurs in our structure. The lattice parameters are similar. {For [1,4-di(*N*-quinoliniummethyl)benzene]$^{2+}$-$[\mathrm{TCNQ}]_3^{2-}$: $a = 7{\cdot}50$, $b = 10{\cdot}07$, $c = 17{\cdot}75$ Å, $\alpha = 102{\cdot}79$, $\beta = 106{\cdot}17$, $\gamma = 98{\cdot}91°$, $Z = 1$.}

Magnetic properties

The EPR spectrum consists of one exchange-narrowed line. Single-crystal EPR measurements show that the angular dependence of the line width can be explained by the assumption of unresolved dipolar interaction (Fig. 8). The solid line is calculated and obeys a $[3\cos^2\theta - 1]^2$ law. A similar dependence has been observed in the charge-transfer compound TMPD–TCNQ, where TMPD is Wurster's Blue (Hoffmann & Hughes, 1970). The angular dependence of the *g* value (Fig. 9) shows that the minimum *g* value appears at an angle where the line width is largest. The minimum *g* value of 2·0022 is normally expected in a position where the molecular planes of the radicals are perpendicular to the external field. This direction coincides fairly well with the direction of maximum dipolar interaction between neighbouring molecules and thus causes the large linewidth.

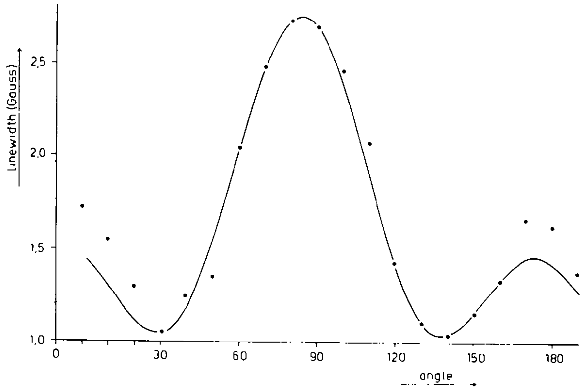

Fig. 8. Angular dependence of the EPR line width for rotation in the *bc* plane. 0° is the *c* axis $\parallel H_0$.

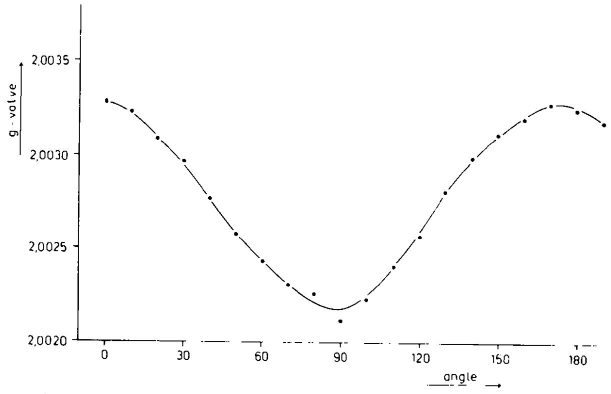

Fig. 9. Angular dependence of the *g* value. Rotation as in Fig. 8.

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 $[Pt(dipy)_2][TCNQ]_2$ 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 $[Pt(dipy)_2][TCNQ]_2$.

This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

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Acta Cryst. (1978). B**34**, 1827–1833

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

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(*Received* 12 *November* 1977; *accepted* 16 *December* 1977)

Bis(malondiamidine)nickel(II) dichloride, $[Ni(C_3H_8N_4)_2]Cl_2$, forms an OD structure. The stacking of orthorhombic layers of molecules results in a monoclinic structure with $a_m = b_m = 16{\cdot}37\ (1)$, $c = 5{\cdot}121\ (3)$ Å, $\gamma_m = 109{\cdot}93\ (4)°$, 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 $R = 8{\cdot}1\%$ (4·8% for the sharp reflections). The ordered structure of bis(malondiamidine)copper(II) diperchlorate $[Cu(C_3H_8N_4)_2](ClO_4)_2$ has been solved at 200 K and refined to $R = 3{\cdot}6\%$. It is monoclinic with $a = 10{\cdot}727\ (4)$, $b = 9{\cdot}719\ (3)$, $c = 7{\cdot}739\ (2)$ Å, $\beta = 92{\cdot}12\ (2)°$, space group $I2/m$. The two structures are very similar. The six-membered chelate rings are in the boat form with metal—NH—C(NH$_2$)—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, $C_2H_7N_5$, (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