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Molecular Complexes Exhibiting Polarization Bonding, X.* The Crystal and Molecular Structure of the 7,7,8,8-Tetracyanoquinodimethane–Bis-(8-hydroxyquinolinato)copper(II) Complex

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The 1:1 complex formed between tetracyanoquinodimethane and bis-(8-hydroxyquinolinato)copper(II) crystallizes as black triclinic crystals, space group $P\bar{1}$, with one molecule of complex in the unit cell of dimensions $a = 12{\cdot}00 \pm 0{\cdot}012$, $b = 7{\cdot}54 \pm 0{\cdot}008$, $c = 7{\cdot}12 \pm 0{\cdot}007$ Å; $\alpha = 112{\cdot}50° \pm 0{\cdot}5°$, $\beta = 88{\cdot}75° \pm 0{\cdot}5°$, $\gamma = 96{\cdot}75° \pm 0{\cdot}5°$. The structure was solved by Patterson methods and refined by least-squares methods using 2651 independent reflexions measured on a linear diffractometer. The final residual, R, was 0·068. The component molecules are stacked in a plane-to-plane manner so that the double bond adjacent to one dicyanomethylene group of the tetracyanoquinodimethane molecule lies over the 5:8 positions of one donor molecule, whilst the other double bond is similarly oriented with respect to the benzenoid ring of the centrosymmetrically related donor molecule. The perpendicular separation of the molecules, in the region of overlap, is approximately 3·2 Å.

Introduction

The powerful electron acceptor tetracyanoquinodimethane (TCNQ) was first shown by Melby, Harder, Hertler, Mahler, Benson & Mochel (1962) to form an unusual set of complexes with metal chelates acting as electron donor components. It was felt that a detailed crystallographic examination of the 1:1 complex formed between TCNQ and bis-(8-hydroxyquinolinato)copper(II) would be of interest to ascertain whether the predominant factor influencing the orientation and packing of the molecules is the charge-transfer interaction between the donor and acceptor, the coordination requirements of the copper atom, or simply general packing requirements. A direct comparison of the

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dimensions of each molecule in the complex with those of the uncomplexed molecules has been made possible by the determinations of Long, Sparks & Trueblood (1965) and Palenik (1964*a*).

Experimental

Crystals of the complex were deposited when boiling solutions of the components in chloroform were mixed and allowed to cool very slowly. The crystals exhibited strong dichroism when examined in plane polarized light, changing from bright green to black as the plane of polarization of the light was rotated.

Weissenberg photographs, using Cu $K\alpha$ radiation ($\lambda = 1\cdot542$ Å), taken about all three crystallographic axes, indicated that the crystals were triclinic. The cell dimensions, determined from the Weissenberg photographs, were refined using a linear diffractometer (Arndt & Phillips, 1961) with Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å). Intensity data for the *hk*0, *hk*1, ..., *hk*7 reciprocal lattice levels were then collected on the linear diffractometer with Mo $K\alpha$ radiation. A total of 2651 independent reflections with $\theta < 32\cdot5°$ were observed out of a possible total of 4300 reflections. Intensity measurements were made with a scintillation counter and a pulse height selector. The moving-crystal stationary-counter technique was employed. The crystal used was approximately cylindrical with a radius of 0·15 mm. No absorption corrections were applied to the data.

Crystal data

$C_{12}H_4N_4.(C_9H_6NO)_2Cu$, $M = 556\cdot1$
Triclinic
$a = 12\cdot00 \pm 0\cdot012$, $b = 7\cdot54 \pm 0\cdot008$, $c = 7\cdot12 \pm 0\cdot007$ Å,
$\alpha = 112\cdot5° \pm 0\cdot5°$, $\beta = 88\cdot75° \pm 0\cdot5°$, $\gamma = 96\cdot75° \pm 0\cdot5°$,
$U = 591\cdot2$ Å^3.
$D_m = 1\cdot600$ g.cm^{-3}, $D_c = 1\cdot608$ g.cm^{-3}.
F(000) = 283.
Mo $K\alpha$ ($\lambda = 0\cdot7107$ Å), $\mu = 10\cdot1$ cm^{-1}.
No systematically absent spectra. Space group $P1$ (no. 1) or $P\bar{1}$ (no. 2). Negative piezoelectric test indicated $P\bar{1}$ and this was confirmed by refinement of the structure.

Determination and refinement of the structure

A trial structure was deduced from the *c*-axis Patterson projection and the structure was partially refined through two cycles of (001) electron density projections followed by *hk*0 structure factor calculations. The value of the usual residual, $R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$, was 0·24.

A three-dimensional Patterson synthesis was then computed. Analysis of the vector distribution confirmed the postulated structure and provided approximate *z* coordinates for the atoms.

Refinement was continued by the block-diagonal least-squares method on an ATLAS computer, with a program written by Dr R. D. Diamand. The weighting scheme $\sqrt{w} = 1$ if $|F_o| < F^*$, otherwise $\sqrt{w} = F^*/|F_o|$ was employed, where $F^* = 40$ on an absolute scale and the scattering factors of Hoerni & Ibers (1954) for carbon, nitrogen and oxygen, and of Freeman & Watson (1961) for copper were used. The reflections too weak to be observed were omitted from the analysis.

After the first cycle of structure-factor least-squares, with anisotropic thermal parameters for copper and isotropic thermal parameters for carbon, nitrogen and oxygen, R had improved to 0·114. A three-dimensional difference Fourier synthesis was calculated from which approximate hydrogen positions were obtained. F^* was changed to 12·5 on an absolute scale as indicated by an agreement analysis. Three further cycles of least squares were calculated, with anisotropic thermal parameters for all the atoms except hydrogen atoms, which were not included in the refinement at this stage. R improved to 0·079. Four more cycles of least squares were then calculated with the inclusion of isotropic hydrogen atoms, thereby giving a total of 210 parameters to be refined. Refinement converged with a final value of R of 0·068, the mean parameter shift being less than one fortieth of a standard deviation. The measured structure factors are compared, in a table† available elsewhere (Williams, 1965) with the values calculated from the penultimate set of atomic parameters.

The final positional parameters, together with their estimated standard deviations obtained from the inverses of the appropriate 3 × 3 matrices from the final cycle of least-squares, are given in Table 1. The bond lengths and angles are shown in Fig. 1.

Table 1. *Final position parameters* (× 10^4) *with* (*below*) *their estimated standard deviations*

	x/a	*y/b*	*z/c*
Cu	0000	0000	0000
	0	0	0
C(1)	0682	2827	4145
	4	6	6
C(2)	1195	3332	6045
	4	6	7
C(3)	1701	1992	6477
	4	6	7
C(4)	1693	0089	5011
	4	6	6
C(5)	2194	−1407	5278
	4	6	7
C(6)	2136	−3185	3716
	4	6	7
C(7)	1607	−3558	1842
	5	6	7
C(8)	1114	−2131	1500
	3	6	6
C(9)	1162	−0288	3124
	3	5	6
O	0594	−2329	−0197
	3	4	5
N(1)	0665	1056	2730
	3	5	5
H(1)	0316	3726	3794
	42	75	80

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† Copies of this table may be purchased from the Science Librarian, University of Nottingham.

Table 1 (*cont.*)

	x/a	y/b	z/c
H(2)	1230	4710	7015
	55	99	106
H(3)	2011	2245	7658
	42	74	79
H(4)	2502	−1308	6671
	56	100	104
H(5)	2480	−4138	3834
	41	72	77
H(6)	1492	−4910	0807
	45	82	83
C(10)	4495	1536	4810
	4	6	7
C(11)	4438	−0310	3158
	3	6	6
C(12)	4959	−1835	3418
	4	6	7
C(13)	3910	−0588	1356
	3	6	7
C(14)	3420	0921	1036
	4	7	7
C(51)	3873	−2378	−0371
	4	7	7
N(2)	3051	2144	0798
	4	8	8
N(3)	3887	−3752	−1787
	4	8	8
H(7)	4203	2474	4507
	41	73	77
H(8)	4823	−3182	2274
	53	94	99

The anisotropic thermal parameters of the atoms (Table 2) were used in an analysis of the rigid-body translational and librational motion (Cruickshank, 1956) of each molecule. The results are given in Table 3 for the TCNQ molecule. The U_{ij}^{obs} of the bis-(8-hydroxyquinolinato)copper(II) molecule could not be explained on the basis of rigid-body translational and librational motion by assuming the centre of motion to be at the molecular centre of symmetry. The r.m.s. discrepancy between the observed and calculated U_{ij} values for the TCNQ molecule is 0·0029 Å^2, or only 8·6%. The method of Busing & Levy (1964) was used to correct the bond lengths of the TCNQ molecule for libration effects.

Table 2. *Final thermal parameters*

Anisotropic values ×10^5; B_{ij} are coefficients in the temperature factor expression $\exp-\{B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk\}$; isotropic values in Å^2; estimated standard deviations in parenthesis.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	482	1017	1406	302	−368	771
C(1)	567	1224	1722	337	−206	943
C(2)	618	1410	1889	308	−262	597
C(3)	598	1714	1552	314	−323	1122
C(4)	402	1523	1623	159	−97	1341
C(5)	536	1651	2065	449	−35	1817
C(6)	516	1649	2222	454	−111	2063
C(7)	578	1162	2226	374	−8	1396
C(8)	510	1192	1818	309	−239	1035
C(9)	382	1308	1458	235	−16	1195
O	819	1264	1665	515	−666	573
N(1)	436	1206	1537	288	−80	866
C(10)	567	1580	1935	572	−60	1547
C(11)	397	1610	1782	378	109	1517
C(12)	529	1461	2073	351	−105	1376
C(13)	481	1849	1784	289	−181	1811
C(14)	595	2180	1863	656	−6	1916
C(15)	532	2120	2030	112	−84	1663
N(2)	896	3164	2805	1059	−178	3209
N(3)	894	2802	2325	444	−178	994

	B		B
H(1)	1·5 (1·0)	H(5)	1·3 (0·9)
H(2)	3·5 (1·4)	H(6)	1·8 (1·0)
H(3)	1·4 (1·0)	H(7)	1·3 (0·9)
H(4)	3·7 (1·5)	H(8)	3·0 (1·4)

Table 3. *Rigid-body thermal parameters for the TCNQ molecule*

(For the molecule centred at $\frac{1}{2},0,\frac{1}{2}$)

$$\tau\dagger = \begin{pmatrix} 299 & 14 & 8 \\ & 317 & 15 \\ & & 403 \end{pmatrix} \times 10^{-4}\,(\text{Å})^2$$

$$\omega\dagger = \begin{pmatrix} 9{\cdot}72 & -1{\cdot}25 & 8{\cdot}38 \\ & 1{\cdot}90 & -5{\cdot}52 \\ & & 22{\cdot}25 \end{pmatrix} \,(^\circ)^2$$

Principal axes:

		Direction cosines† (×10^4) relative to		
	Eigenvalue	a	b'	c^*
τ	0·0406 (Å)^2	948	1826	9786
	0·0321	4739	8562	−2056
	0·0291	7855	−4833	54
ω	25·3 (°)^2	4256	−2093	8804
	5·9	8949	2418	−3751
	0·4	−1344	9475	2902

U_{ij} (Å^2)×10^4†‡

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(10)	392	350	442	70	−14	6
	−4	14	−20	23	−11	10
C(12)	399	354	428	51	−17	−16
	−2	2	25	−1	−13	1
C(11)	301	350	406	10	6	25
	−24	18	−15	24	3	2
C(13)	308	444	416	−2	−1	53
	32	−39	−25	32	−53	11
C(14)	394	530	492	77	−24	110
	11	−40	−82	14	5	−41
C(15)	416	569	417	−10	−30	1
	−24	−61	26	−19	0	21
N(2)	599	635	611	212	−77	145
	9	39	2	−38	9	2
N(3)	619	739	445	43	−78	−83
	2	43	65	−16	44	3

† Referred to directions of the orthogonal axes a,b',c^* (where b' is perpendicular to a and c^*).

‡ The numbers below the U_{ij} are the differences (×10^4) of U_{ij} derived from B_{ij} and those calculated from rigid-body parameters. The r.m.s. difference is 0·0029 (Å^2). The estimated standard deviation of U_{ij} is 0·0033 (Å^2).

Least-squares planes, one for each molecule, were calculated by the modification (Blow, 1960) of the method of Schomaker, Waser, Marsh & Bergman (1959). Each plane was defined by all the atoms, except hydrogen, of one molecule and each atom included was given unit weight. The least-squares plane through the quinonoid ring and that through the dicyanomethylene group of the TCNQ molecule were also calculated because the TCNQ molecule, as a whole, showed significant deviations from planarity. The results of these calculations are shown in Table 4.

Description and discussion of the structure

A noticeable feature of the complex is the square-planar distribution of atoms about the copper atom. This is formed by two Cu–N bonds of length 1·946 Å and two Cu–O bonds of length 1·926 Å. No other atoms, apart from those of the directly bonded hydroxyquinolinato

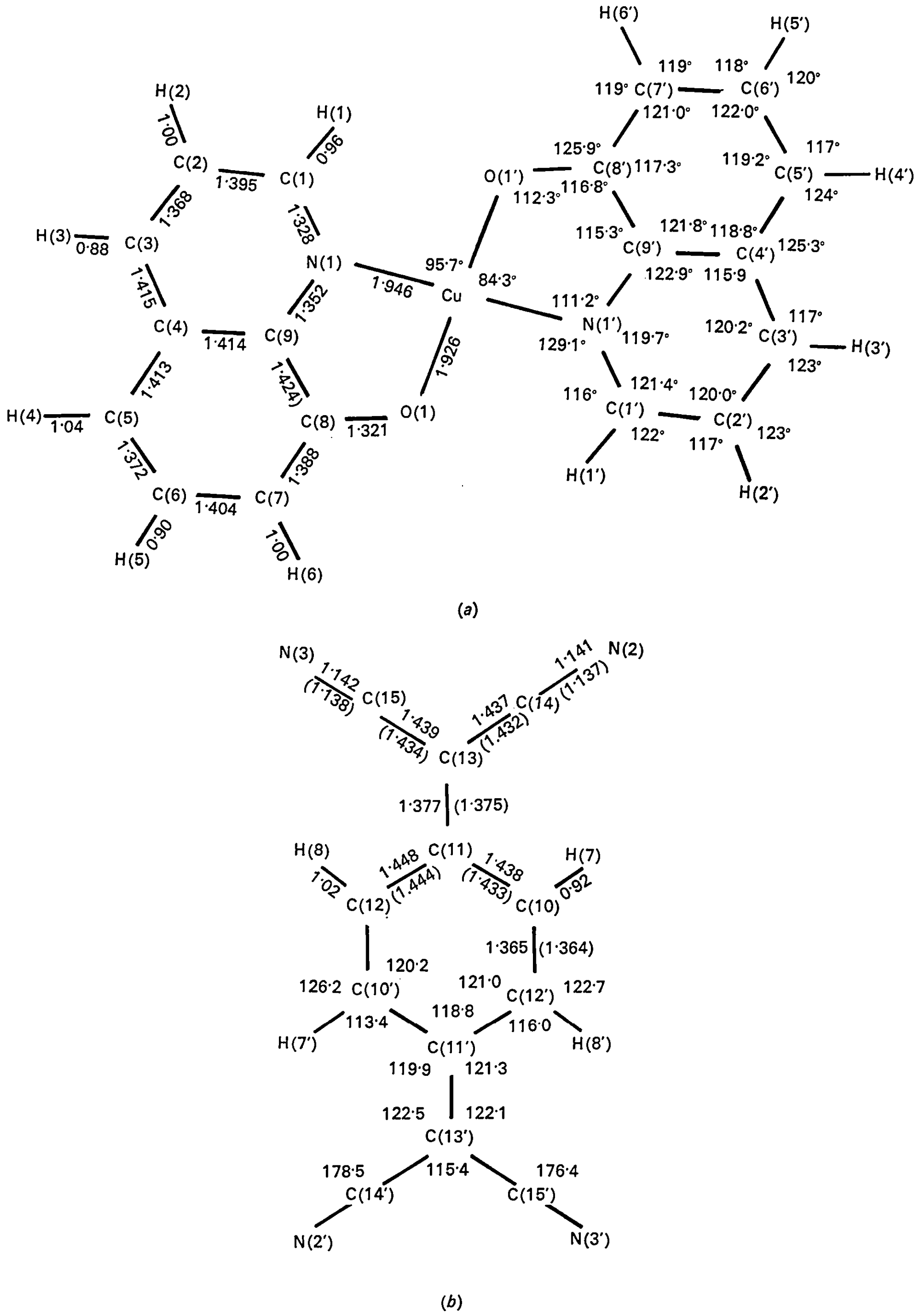

Fig. 1. Molecular dimensions: (*a*) bis-(8-hydroxyquinolinato)copper(II), (*b*) TCNQ (bond lengths in parentheses are before correction for libration). Standard deviations for bonds to Cu are 0·003 Å and 0·3°; for bonds between C, N or O are 0·005–0·008 Å and 0·4–0·6°; for bonds to H are 0·06–0·08 Å and 4°.

groups, approach nearer than 3·8Å to the copper atom, so the usual tendency to octahedral coordination is not found in this structure. This differs from the situation in the *β* form of anhydrous bis-(8-hydroxyquinolinato)copper(II) (Palenik, 1964*a*) where the copper atom has, in addition, a fifth bond of 2·830 Å to an oxygen atom of an adjacent molecule. The arrangement of the molecules in the TCNQ complex is therefore not determined by the coordination requirements of the copper atom and the importance of the other structural requirements is indicated by the fact that the copper coordination sphere is not completed.

The N(1)–Cu–O interbond angle of 84·3° is in good agreement with that of 84·6° obtained by Palenik (1964*a*) in the investigation of the structure of anhydrous copper oxinate. The mean of the two Cu–O bond lengths determined by Palenik (1964*a*) agrees to within 0·004 Å of the value obtained in the present study, but the Cu–N(1) bond length of 1·946 Å in the present study differs very significantly from that of 1·973 Å in the uncomplexed molecule. This variation of five standard deviations might be because the copper atom has a distorted tetragonal pyramidal coordination in the uncomplexed state, but has a square-planar configuration in the present study. The square-planar copper atom might be expected to form slightly shorter bonds than the tetragonal pyramidal copper atom, although why the Cu–O bond is not also shortened on formation of the complex is not clear.

The component molecules are stacked in a plane-to-plane manner – a common feature of this type of molecular complex (Wallwork, 1961). Fig. 2 shows the structure projected along the *b* axis, and Fig. 3 is a view perpendicular to the mean molecular planes, showing how the molecules overlap in such a way that each dicyanomethylene group of the TCNQ molecule lies directly over or under the benzenoid ring of the hydroxyquinolinato group of a donor molecule. Intermolecular interaction appears to take place between these pairs of groups, but since these pair-wise interactions take place at both ends of each molecule, they link the molecules into infinite chains. Direct evidence of the interaction between the TCNQ molecule and the oxinate molecule is provided by four interatomic distances, between the component molecules, which are considerably shorter than the sum of the expected van der Waals radii of aromatic systems. These approaches (C(5)–C(11) 3·236 Å, C(9)–C(14) 3·267 Å, C(7)–C(15) 3·314 Å, N(1)–N(2) 3·303 Å) are illustrated in Fig. 2 together with some other interatomic distances between adjacent molecules. It is interesting to note that the TCNQ–TCNQ distances and oxinate–oxinate distances are approximately 3·4 Å, and this may be taken as an internal standard with which to compare the four close approaches between TCNQ and oxinate molecules. Calculations by Long, Sparks & Trueblood (1965) indicate that the atoms C(11), C(14) and C(15) are the most electron deficient atoms in the Hückel molecular orbital model of the TCNQ molecule. It is therefore probably not a coincidence that it is these three atoms which have the shortest contacts to the donor molecule of the complex.

Comparison of the bond lengths of the hydroxyquinolinato group in the present study with the corre-

Table 4. *Molecular least-squares planes*

Description of plane

I Complete bis-(8-hydroxyquinolinato)copper(II) molecule.
II Complete TCNQ molecule.
III Quinonoid ring of TCNQ molecule [C(10), C(11), C(12), C(10′), C(11′), C(12′)].
IV Dicyanomethylene group of TCNQ molecule [C(11), C(13), C(14), C(15), N(2), N(3)].

	Direction cosines of planes relative to *a**	*b*	*c′*	Perpendicular distance of plane from origin
I	0·8674	0·3541	−0·3496	0·000 Å
II	0·8724	0·3694	−0·3201	3·315
III	0·8611	0·3669	−0·3520	3·148
IV	0·8857	0·3628	−0·2896	3·389

	Distance from plane I		Distance from plane I
Cu	0·000 Å	C(4)	−0·015 Å
O	−0·030	C(5)	−0·012
N(1)	0·007	C(6)	−0·011
C(1)	0·015	C(7)	0·006
C(2)	0·007	C(8)	0·017
C(3)	0·002	C(9)	0·003

	Distance from plane II	III	IV
C(10)	−0·010	−0·002	0·091
C(11)	−0·043	0·002	0·028
C(12)	−0·038	−0·002	0·057
C(13)	−0·057	0·032	−0·033
C(14)	−0·016	0·083	−0·015
C(15)	−0·029	0·098	−0·034
N(2)	0·038	0·144	0·022
N(3)	0·062	0·220	0·033

sponding weighted mean bond lengths from the two accurate determinations to date (Palenik, 1964*a*,*b*) yielded a r.m.s. discrepancy of 0·010 Å. This discrepancy improves to 0·007 Å, or one standard deviation, if the bond length C(6)–C(7) is omitted. The C(6)–C(7) bond length of the present study differs by 0·024 Å from the weighted mean described above, and by 0·031 Å (three standard deviations) from the weighted mean of the two values found in bis-(8-hydroxyquinolinato)copper(II) (Palenik, 1964*a*). This difference is further discussed below. The mean deviation of the interbond angles in the copper oxinate molecule of the present study and those of the uncomplexed molecule is 0·8°, *i.e.* approximately one standard deviation. The greatest difference involves the angle C(4)–C(5)–C(6) which is 119·2° in the present study as compared with angles of 120·8 and 121·3° in the uncomplexed molecule (Palenik, 1964*a*). This difference is significant at the 0·01 confidence level.

Comparison of the weighted means of chemically equivalent but crystallographically independent bond lengths of the TCNQ molecule in the complex with corresponding bond lengths in the uncomplexed molecule (Long, Sparks & Trueblood, 1965), corrected in both cases for the effects of molecular libration, shows very good agreement, apart from the C(10)–C(12′) bond, which is 0·021 Å longer in the present determination than in the uncomplexed state. This is a difference of 2·5σ and is therefore at the border of significance. The central ring of the TCNQ molecule may thus be considered as slightly less quinonoid – or more benzenoid – in the complex than it is in the uncomplexed state. Excluding the C(10)–C(12′) bond length, the r.m.s. agreement between the weighted means of the chemically equivalent bond lengths in the two determinations is better than 0·003 Å, *i.e.* approximately 0·5σ.

The TCNQ molecule is definitely non-planar as shown by the deviations of the atoms from the mol-

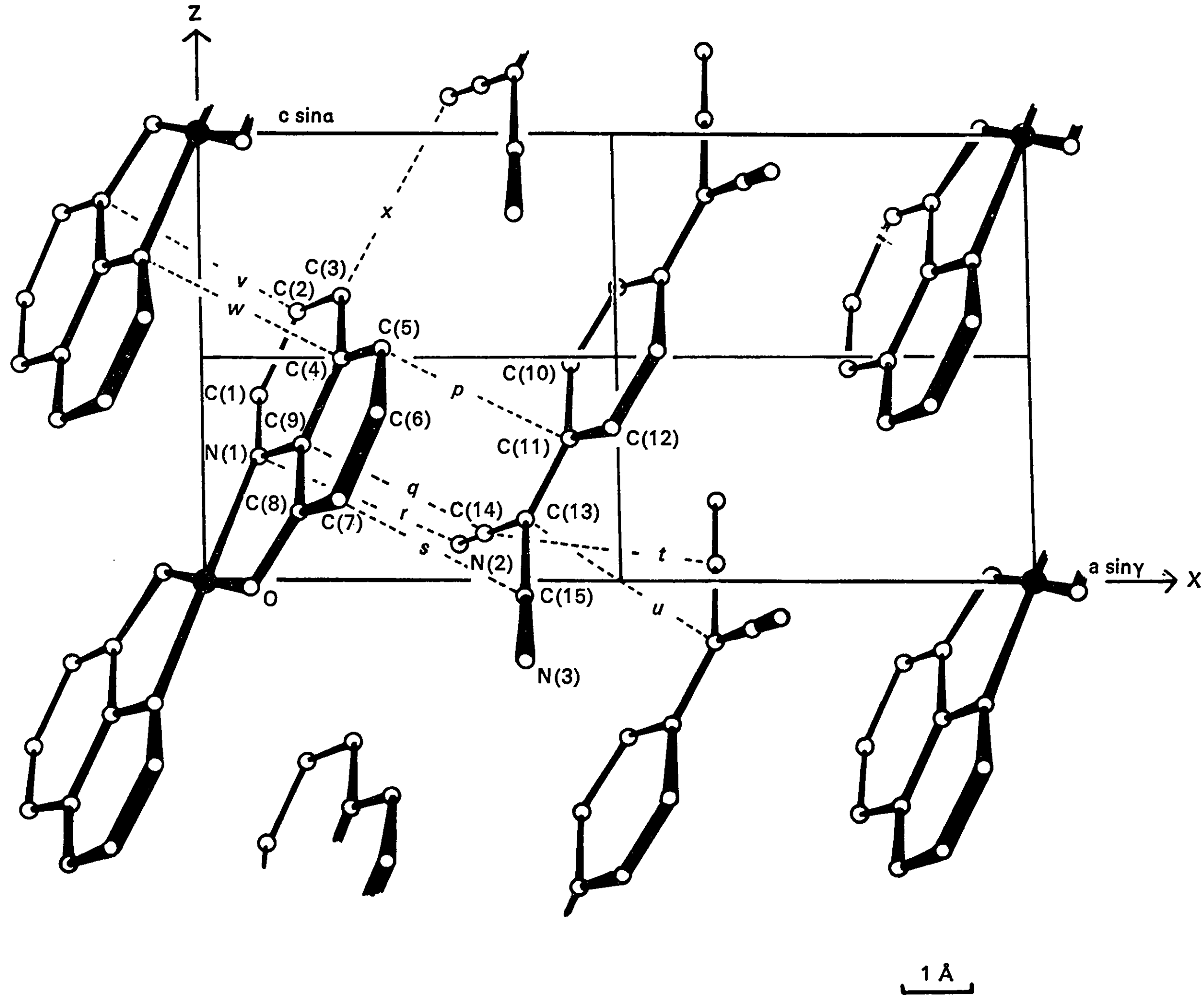

Fig. 2. The structure projected along the *b* axis, showing short intermolecular contacts. The distances (Å) indicated are: $p=3\cdot236$, $q=3\cdot267$, $r=3\cdot303$, $s=3\cdot314$, $t=3\cdot387$, $u=3\cdot451$, $v=3\cdot457$, $w=3\cdot410$, $x=3\cdot467$, all ± *ca.* 0·007 Å.

ecular least-squares plane (Table 4, plane II). This is in contrast with the planar molecule found by Long, Sparks & Trueblood (1965). The central quinonoid ring, however, is planar in the present study, no atom deviating from the mean plane by more than 0·5σ. The dicyanomethylene group deviates significantly from planarity because the C–C≡N groups are not linear, but have angles of 176·4 and 178·5° at the central carbon atoms. The dicyanomethylene group as a whole is not coplanar with the quinonoid ring, and the TCNQ molecule therefore exhibits non-planarity at the three atoms C(11), C(14) and C(15). It is to be noted that it is these three atoms which are involved in the close contacts with the bis-(8-hydroxyquinolinato)copper(II) molecule.

The bis-(8-hydroxyquinolinato)copper(II) molecule does not exhibit any marked non-planarity, apart from the oxygen atom, which lies 0·030 Å from the mean molecular plane. This deviation is discussed below in conjunction with the thermal motion of this molecule.

The observed thermal motions of the TCNQ molecule are interesting in that they are almost identical with those of the uncomplexed molecule (Long, Sparks & Trueblood, 1965). This was quite unexpected, as it may be assumed that the environment of a molecule plays a large part in determining the thermal parameters of the atoms. The principal axes of the vibration ellipsoid of the TCNQ molecule, considered as a rigid body, are of dimensions 0·0406, 0·0321 and 0·0291 Å^2 in the present study as compared with 0·0435, 0·0342 and 0·0299 Å^2 for the uncomplexed molecule. The overall vibration ellipsoid is not markedly anisotropic and its major axes are almost parallel to the natural crystal axes. The principal axes of the libration ellipsoid of the TCNQ molecule in the complex have dimensions 5·0, 2·4 and 0·6° as compared with dimensions of 5·4, 2·3 and 1·6° in the uncomplexed molecule. In both cases, the libration is greatest about an axis which almost coincides with the long axis of the molecule.

No interpretation of the thermal parameters, U_{ij}, of the bis-(8-hydroxyquinolinato)copper(II) molecule can be advanced on the basis of rigid-body motions. Internal molecular vibrations must be playing a predominant rôle in the overall thermal motion of the molecule. The oxygen atom does exhibit marked anisotropy of thermal motion, U_{11} for this atom being almost twice as large as either U_{22} or U_{33}. It might also be significant that this atom deviates from the mean plane through the molecule by 0·030 Å (8σ). The direction of displacement of this oxygen atom is in almost the same direction as U_{11}.

Examination of the overlap of the donor and acceptor molecules (Fig. 3) reveals a marked similarity to the overlap of the constituent molecules in the 1:1 complex formed between tetracyanoethylene and naphthalene (part IX, Williams & Wallwork, 1967; Prout & Wallwork, 1966). The ethylenic double bond [C(11)–C(13)] of the TCNQ molecule lies in a parallel plane above two carbon atoms, which are diametrically opposite each other in the benzenoid ring of the donor molecule, bis-(8-hydroxyquinolinato)copper(II). This would lead to shifts of the π-orbital electrons in the molecules with a consequent slight alteration in bond lengths and angles, especially in the region of the close molecular approaches. The differences between the bond lengths and angles of the molecules in the complex and those of the uncomplexed molecules are in the directions expected on the basis of this type of interaction. Application of multiparameter significance tests (Cruickshank & Robertson, 1953) on the bond length differences show them to be in the 'possibly significant' range.

General conclusions

This work shows, in two ways, evidence of interaction between the component molecules of the complex. Firstly, there is the plane-to-plane stacking, which is now recognized as a common feature in structures of the π–π charge-transfer type, with an average perpendicular distance between the planes of approximately 3·2 Å, which is less than a normal van der Waals separation. Secondly, there appears to be a specific interaction between the dicyanomethylene group of TCNQ and the benzenoid ring of the oxinate, which is of the same type as that found in the structure of the complex between tetracyanoethylene and naphthalene (part IX, Williams & Wallwork, 1967) and results in four short interatomic contacts between these groups. It is noticeable that the molecular overlap is not of the more usual ring-to-ring type, but is such as to allow each dicyanomethylene group to take part in this more specific type of interaction.

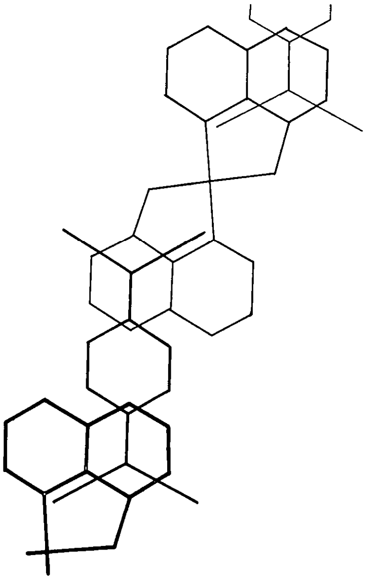

Fig. 3. Molecular overlap as viewed in a direction perpendicular to the mean molecular planes.

It is believed that this is the first case in which an accurate comparison of molecular dimensions can be made for each component in a complex with the same molecule in an uncomplexed state. This comparison shows that, even in this case where there is some specific interaction between the components, there is very little change in molecular dimensions on forming the complex. It is fairly certain, therefore, that interactions of a more general nature, which bind the components in weaker π–π complexes, will have negligible effects on the dimensions of the molecules involved.

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Position and Thermal Parameters of Oxygen Atoms in Sodium Nitrate*

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The thermal and position parameters of the oxygen atoms in sodium nitrate, at room temperature and at intervals up to 200°C, have been determined. Intensities of reflections to which only the oxygen atoms contribute were measured carefully by film and counter techniques. The N–O bond length, uncorrected for thermal effects, is 1·241 ($\sigma = 0{\cdot}002$) Å at 25°C and appears to decrease progressively as the temperature is raised. This effect is attributed to increasing libration of the nitrate groups about threefold axes in the crystal.

Introduction

Sodium nitrate crystallizes in the rhombohedral subgroup of the trigonal system in space group $R\bar{3}c$, with two formula units of $NaNO_3$ per unit cell. The nitrogen and sodium atoms lie on threefold axes, the former at 0,0,0 and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, and the latter at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$, and $\frac{3}{4},\frac{3}{4},\frac{3}{4}$. The three oxygen atoms of each nitrate group are arranged symmetrically about the nitrogen atoms in planes normal to the threefold axes; each oxygen atom lies on a twofold axis. Successive nitrate groups are rotated 60° relative to one another as shown in Fig. 1.

The atomic arrangement in crystalline $NaNO_3$ differs from a completely body centered one only by virtue of rotations of successive nitrate groups by 60° about the body diagonal of the unit cell. Only the oxygen atoms therefore contribute to reflections of the type $h+k+l=2n+1$.

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