are in the Cp* ring while C(51)–C(55) are the corresponding CH_3 groups. The six-membered-ring atoms are Ir(2), S(2) and C(32)–C(35); C(31) and C(36) are the CH_3 carbons attached to C(32) and C(35), respectively; the CO ligand consists of C(61) and O(61).

The most notable feature of the structure is the six-membered ring. In the molecule Cp*Ir(*S,S*-2,5-Me_2T), which does not contain a CO ligand, this ring is planar and the three C—C distances in it are the same within experimental error (Chen, Daniels & Angelici, 1990*b*). These distances, together with other data, were interpreted to indicate that the six-membered ring in Cp*Ir(*C,S*-2,5-Me_2T) is a π-delocalized system (Chen, Daniels & Angelici, 1990*a*). In Cp*Ir(CO)(*C,S*-2,5-Me_2T), the C—C bond distances have alternating lengths with C(2)—C(3) and C(4)—C(5) being short (1.34 Å) as compared with C(3)—C(4) (1.47 Å). This indicates localized π bonding at C(2)—C(3) and C(4)—C(5). Moreover, the six-membered ring is no longer planar as shown by the fact that C(5) is 0.30 Å above the plane defined by S(1), C(1), C(2), C(3), C(4) toward Ir(1), while the Ir(1) is 1.19 Å out of this plane. These distortions from planarity are similar to those in the PMe_2Ph analog, Cp*Ir(PMe_2Ph)(*C,S*-2,5-Me_2T), which was also assigned a π-localized structure. Although the bond distances in Cp*Ir(CO)(*C,S*-2,5-Me_2T) and Cp*Ir(PMe_2Ph)(*C,S*-2,5-Me_2T) are the same within experimental error, the Ir is further (1.19 *versus* 0.69 Å) out of the plane defined by S(1), C(1), C(2), C(3), C(4) in Cp*Ir(CO)(*C,S*-2,5-Me_2T).

Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division. We thank Johnson Matthey, Inc. for the loan of iridium.

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Acta Cryst. (1992). C**48**, 2122–2124

Structure of Copper(II) 3-Cyanobenzoate

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(*Received* 28 *October* 1991; *accepted* 6 *March* 1992)

Abstract. [Cu($C_8H_4NO_2$)$_2$], $M_r = 355.8$, triclinic, $P\bar{1}$, $a = 6.545$ (4), $b = 10.235$ (5), $c = 12.174$ (6) Å, $\alpha = 74.40$ (3), $\beta = 85.02$ (4), $\gamma = 78.64$ (3)°, $V = 769.6$ (7) Å^3, $Z = 2$, $D_x = 1.535$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.440$ mm^{-1}, $F(000) = 358$, room temperature, $R = 0.029$ for 1213 unique reflections having $|F| > 4\sigma(|F|)$. The Cu atoms are coordinated by four O atoms from four carboxylate groups, one N atom from a cyano substituent and another Cu atom in a distorted octahedral arrangement. There are six coordination distances: four of 1.957 (3), 1.964 (3), 1.965 (3) and 1.975 (3) Å with the four carboxylate O atoms, one of 2.191 (4) Å with the N atom, and the largest of 2.664 (2) Å with the neighbouring Cu atom. The dimeric units formed by Cu-atom pairs are linked through the aromatic ligands building a polymeric chain structure.

Introduction. In the course of our studies on copper(II) arylcarboxylates (Cueto, Gramlich, Petter, Rys

& Rys, 1991), we have prepared copper(II) 3-cyanobenzoate (CuCNB) and determined its crystalline structure. The complex is a polymer formed by chains of aromatic ligands held together through bridges of Cu-atom pairs coordinated to the ligands through the O and N atoms of the aromatic nuclei. This structure combines features of the typical copper(II) carboxylate dimers (van Niekerk & Shoening, 1953) and others of copper polymeric complexes (Valentine, Silverstein & Soos, 1974; Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1981; Bakalbassis, Bozopoulos, Mrozinski, Rentzeperis & Tsipis, 1988; Bencini, Benelli, Fabretti, Franchini & Gatteschi, 1986). CuCNB shows the same core as the copper(II) acetate monohydrate, but the presence of a cyano group in the 3 position of the aromatic ring allows the structure to become polymeric. Furthermore, there are two types of 3-cyanobenzoate molecules, those that are coordinated to Cu through O and N atoms and those which are not bridging molecules and are only coordinated to Cu through O atoms; both types can also be recognized in the IR spectrum (cyano peaks: 2260, 2220 cm^{-1}).

Experimental. CuCNB was synthesized from solid sodium 3-cyanobenzoate and copper(II) sulfate pentahydrate at room temperature, in aqueous medium by a diffusion-controlled reaction method (Date, Yamazaki, Motokawa & Tazawa, 1970). A homogeneous complex formed by small green–blue crystals was generated. Only one crystal morphology was formed. The crystals were washed with water and air dried. The structural formula was determined from microanalysis data: C 53.69, H 2.25, N 7.83%. These are in close agreement with the calculated values for $Cu[(3\text{-}CN)C_6H_4COO]_2$: C 54.01, H 2.26, N 7.87%.

A small crystal of about 0.1 × 0.1 × 0.1 mm was chosen for the structure determination. Intensity measurements were carried out at room temperature with a Picker automated single-crystal diffractometer upgraded by Stoe, using monochromatic Mo $K\alpha$ radiation. Unit-cell constants were calculated from 26 reflections with $15 < 2\theta < 22°$. Intensity data were measured for 1441 reflections with $h_{\max} = \pm 6$, $k_{\max} = \pm 9$, $l_{\max} = 11$ and 2θ values in the range $3 < 2\theta < 40°$ using a 2θ–θ scan. Profile fitting was carried out by a learnt-profile method (Clegg, 1981). One standard reflection (104) was measured at time intervals of 60 min. No decay of intensities was observed. For the data reduction, software of Stoe (Stoe Corporation, 1987) was used. On the basis of ψ-scan measurements of selected reflections, absorption corrections were omitted.

Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* ($Å^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cu	−0.1386 (1)	−0.0834 (1)	0.5344 (1)	24 (1)
O(1)	0.0612 (5)	−0.2133 (3)	0.4656 (3)	38 (1)
O(2)	0.2908 (5)	−0.0707 (3)	0.4078 (3)	34 (1)
O(3)	0.0255 (5)	−0.1483 (3)	0.6726 (3)	40 (1)
O(4)	0.2516 (5)	−0.0026 (3)	0.6176 (3)	33 (1)
N(1)	0.3342 (6)	−0.7599 (4)	0.3977 (3)	32 (2)
N(2)	0.1207 (9)	−0.4979 (6)	1.1385 (5)	76 (2)
C(11)	0.2311 (7)	−0.1834 (5)	0.4192 (3)	27 (2)
C(12)	0.3759 (6)	−0.2934 (4)	0.3775 (3)	23 (2)
C(13)	0.3163 (7)	−0.4191 (4)	0.3865 (3)	25 (2)
C(14)	0.4561 (7)	−0.5257 (4)	0.3568 (4)	24 (2)
C(15)	0.6561 (7)	−0.5080 (5)	0.3165 (4)	29 (2)
C(16)	0.7154 (7)	−0.3833 (4)	0.3068 (4)	30 (2)
C(17)	0.5773 (7)	−0.2769 (4)	0.3377 (3)	28 (2)
C(18)	0.3901 (7)	−0.6571 (5)	0.3755 (4)	27 (2)
C(21)	0.1778 (7)	−0.0977 (4)	0.6886 (4)	26 (2)
C(22)	0.2780 (7)	−0.1582 (4)	0.8009 (4)	31 (2)
C(23)	0.1934 (7)	−0.2574 (5)	0.8838 (4)	35 (2)
C(24)	0.2832 (8)	−0.3148 (5)	0.9879 (4)	43 (2)
C(25)	0.4628 (10)	−0.2729 (6)	1.0109 (5)	61 (3)
C(26)	0.5467 (9)	−0.1751 (6)	0.9306 (5)	62 (3)
C(27)	0.4561 (8)	−0.1168 (5)	0.8240 (4)	43 (2)
C(28)	0.1931 (9)	−0.4177 (6)	1.0712 (5)	53 (2)

For the structure solution, 1441 unique reflections were measured, of which 1213 were taken as observed [$|F| > 4\sigma(|F|)$]. Neutral complex scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 71) were used. The crystal structure could be easily solved using *SHELXTL-Plus* software (Sheldrick, 1988) with the heavy-atom method. The H atoms were generated by routine calculation by the *SHELXTL-Plus* software. Final refinement based on $|F|$ (1441 reflections, 208 parameters) resulted in $R = 0.029$, $wR = 0.041$ for the observed reflections, $S = 1.05$, with isotropic atomic displacement parameters for H atoms and anisotropic atomic displacement parameters for non-H atoms. Weights were assigned as $w = 1/[\sigma^2(|F|) + 0.0012|F|^2]$; $(\Delta/\sigma)_{\max} = 0.2$; $(\Delta\rho)_{\max} = 0.31$, $(\Delta\rho)_{\min} = -0.25$ e Å^{-3}.

The final values of the atomic coordinates, isotropic and anisotropic displacement parameters and their e.s.d.'s are given in Table 1.* A view of the asymmetric unit and of two symmetry-related units is shown in Fig. 1.

Discussion. The crystal structure of CuCNB encompasses two features:

(i) The Cu atoms are arranged in pairs held together by a core of eight O atoms belonging to four different carboxylate groups. Such dimeric units have also been found in the crystal structures of copper(II) acetate monohydrate (van Niekerk &

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* Lists of observed and calculated structure factors, anisotropic displacement parameters of the non-H atoms and atomic and isotropic displacement parameters of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55282 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BX0579]

Shoening 1953), and of arylcarboxylates like copper(II) *o*-bromobenzoate (Harrison, Rettig & Trotter, 1972) and copper(II) *o*-methoxybenzoate monohydrate (Adelsköld, Eriksson, Werner, Westdahl, Lucanska, Krätsmar-Smogrovic & Valent, 1989). In these complexes the distance between the Cu atoms within the dimeric units lies in the range 2.6–2.75 Å. In the case of CuCNB this distance is 2.664 (2) Å.

(ii) Remarkably, in CuCNB these pairs are linked together by two 3-cyanobenzoate molecules unlike in the case of the above-mentioned copper(II) carboxylates, where the pairs of Cu atoms are isolated from each other. Four of the eight carboxylate O atoms of one dimeric unit belong to two 3-cyanobenzoate ligands, the cyano substituents of which are each coordinated to another neighbouring dimeric copper unit. This arrangement leads to a polymeric framework consisting of parallel double-chains. The individual double-chain is formed by two chains of aromatic nuclei which run in opposite directions and intersect repeatedly at the dimeric copper units. A packing plot of the polymeric chains along the *x* axis is shown in Fig. 2.

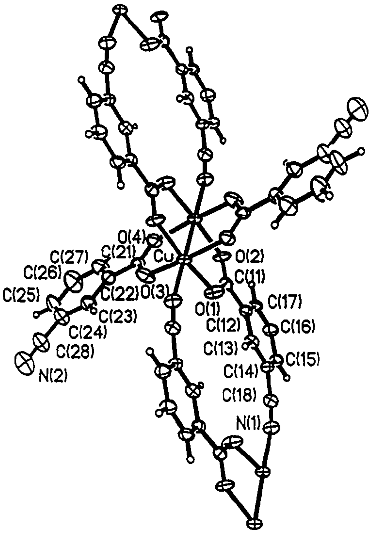

Fig. 1. View of the asymmetric unit and of two symmetry-related units of copper(II) 3-cyanobenzoate.

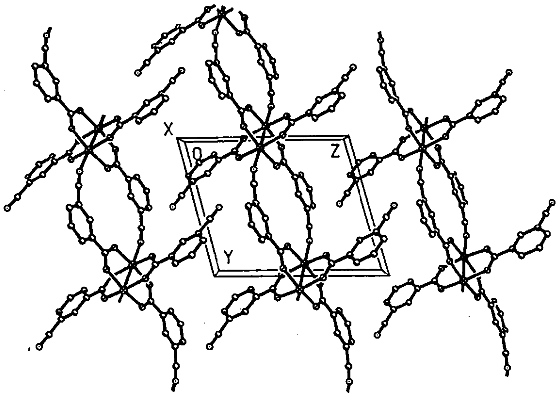

Fig. 2. Packing plot of the polymeric chains along the *x* axis. The extension of the unit cell in perspective view is also shown.

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

Cu—Cu^{i}	2.664 (2)	O(1)—Cu—O(4^{i})	88.0 (1)
Cu—O(1)	1.975 (3)	O(4^{i})—Cu—O(2^{i})	91.2 (1)
Cu—O(3)	1.965 (3)	O(2^{i})—Cu—O(3)	89.4 (1)
Cu—O(2^{i})	1.957 (3)	O(3)—Cu—O(1)	88.7 (1)
Cu—O(4^{i})	1.964 (3)	O(1)—Cu—Cu^{i}	85.0 (1)
Cu—N(1^{i})	2.191 (4)	Cu^{i}—Cu—N(1^{i})	172.7 (1)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The only known copper arylcarboxylate with a similar structure to CuCNB is the copper(II) aspirinate whose dimeric units are bonded through the O atom of the acetyl residue (Manojlovic-Muir, 1967). In CuCNB the coordination polyhedron of Cu is formed by four carboxylate O atoms in a plane of four aromatic ligands, the N atom of the cyano substituent of the fifth aromatic nuclei as terminal ligand, and another Cu atom occupying the sixth coordination position.

Selected interatomic distances and angles in the coordination polyhedra around Cu are given in Table 2.

This work was supported by the Schweizerischer Nationalfonds zur Förderung wissenschaftlicher Forschung under Grant No. 2000-5.478.

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