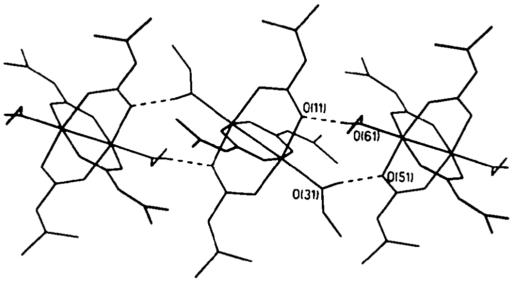

Fig. 2. The hydrogen bonding between ethanol and carboxylate ligands.

and, unless otherwise stated, structural parameters quoted below are averages over all relevant ligands in both dimers.

The metal separation [2·594 (2) Å] is within the normal range for tetrakis(μ-carboxylato)-dicopper(II) complexes; the Cu atoms lie 0·185 Å from the plane (r.m.s. $\Delta = 0{\cdot}002$ Å) defined by their four coordinating carboxylate O atoms, displaced towards the axial ethanol ligands. The bidentate 3,3′-dimethylacrylate bridges are slightly distorted; Cu—O bonds involving O atoms participating in intermolecular hydrogen bonding are approximately 0·02 [O(51)] and 0·03 Å [O(11)] larger than the other Cu—O bonds [1·957 (3) Å]. Distortion of this type and magnitude has been reported for tetrakis(μ-acetato)-bis(methanol)dicopper(II) (Rao, Sathyanarayana & Manohar, 1983) in which binuclear copper(II) units also link *via* intermolecular hydrogen bonding to form chains. The Cu—O(alcohol) bond lengths for that complex [2·160 (3) Å] and for tetrakis[μ-(2,2,5,5-tetramethyl-1-oxo-dihydropyrrole-3-carboxylato)]-bis(ethanol)dicopper(II) (2·17 Å) (Gusejnova & Mamedov, 1978) show close agreement with the values presented here [2·155 (4) Å]. This is expected since the coordination geometry around the Cu atom in each complex approximates to square pyramidal; the bond lengths are roughly 0·35 Å shorter than those between Cu^{II} and O(ethanol) where the ethanol molecule forms part of an axially distorted octahedral coordination sphere around the Cu^{II} (Muhonen, Pajunen & Hämäläinen, 1980).

There is no coordination of the carboxylate side-chain double bonds to the Cu atoms, and no significant intermolecular double-bond interaction.

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Structure of Diformatobis(2-methylbenzimidazole)copper(II)

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Abstract. $[Cu(CHO_2)_2(C_8H_8N_2)_2]$, $M_r = 417{\cdot}91$, monoclinic, $P2_1/n$, $a = 6{\cdot}3306\ (5)$, $b = 13{\cdot}4855\ (11)$, $c = 11{\cdot}1863\ (5)$ Å, $\beta = 105{\cdot}471\ (5)°$, $V = 920{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}508$, $D_m = 1{\cdot}515$ Mg m^{-3}, λ(Cu $K\alpha$) $= 1{\cdot}541840$ Å, $\mu = 1{\cdot}91$ mm^{-1}, $F(000) = 430$, room temperature, final $R = 0{\cdot}0391$ for 1877 reflections. The

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structure is monomeric. The formate ions and 2-methylbenzimidazole molecules act as monodentate ligands forming two Cu—O bonds of 1·985 (1) Å and two Cu—N bonds of 1·971 (1) Å. The coordination around copper is square planar, with long apical Cu—O contacts of 2·668 (1) Å. The crystal structure is stabilized by relatively strong intermolecular hydrogen bonds between the semicoordinating formate oxygen atoms and the N—H atoms of neighbouring 2-methylbenzimidazole ligands [O···N 2·763 (2) Å].

Introduction. It has long been recognized that copper(II) formate and its adducts differ in structural and magnetic properties from other copper(II) carboxylates (Doedens, 1976). The crystal structure of the adduct [$CuL_2(CHO_2)_2(H_2O)$], where L = benzimidazole, has been determined (Bukowska-Strzyżewska & Tosik, 1983). This compound contains bridging water molecules.

Two crystal structures of dimeric copper(II) formate adducts with additional ligands are also known (Yawney & Doedens, 1970; Goodgame, Hill, Marsham, Skapski, Smart & Troughton, 1969). These adducts [$Cu(CHO_2)_2L$], where L = urea and thiocyanate, respectively, are structurally related to copper(II) acetate monohydrate (Van Niekerk & Schoening, 1953), with four bidentate carboxylate anions bridging the copper ions. We now report the first crystal structure of a monomeric copper(II) formate adduct, found coincidentally during the investigation of ligand-induced BF_4-decomposition reactions in the presence of triethylorthoformate (Ten Hoedt & Reedijk, 1981).

Experimental. Warm solutions of 2 mmol of copper(II) tetrafluoroborate and 8 mmol of 2-methylbenzimidazole in 20 ml ethanol were mixed, and 5 ml triethylorthoformate added. On filtration purple crystals were obtained, which were washed with ethanol and diethyl ether, and dried *in vacuo*. Composition: calculated for $C_{18}H_{18}CuN_4O_4$: Cu 15·2, C 51·73, H 4·34, N 13·4, O 15·3%; found: Cu 15·5, C 51·70, H 4·40, N 13·4, O 15·1%. The above compound could also be obtained from equimolar amounts of copper(II) formate and 2-methylbenzimidazole in a 1:1 mixture of water and ethanol, the synthesis of which is analogous to the preparation of [$Cu(benzimidazole)(CHO_2)_2(H_2O)$] (Bukowska-Strzyżewska & Tosik, 1983).

Crystal size 0·13 × 0·15 × 0·37 mm; D_m by flotation in $CHCl_3/C_2H_2Br_2$, Weissenberg photographs; intensity data collected in ω–θ scan mode, $2·5 < \theta < 75°$, Enraf–Nonius CAD-4 four-circle diffractometer (graphite-monochromated Cu $K\alpha$ radiation); 1877 independent reflections measured, index range h 0/7, k 0/16, l −14/13; 242 reflections not significant with $I < 2\sigma(I)$; three standard reflections measured after every 60 reflections, 6·5% decay; $R_{\text{int}} = 0·0068$; correction for Lorentz and polarization effects; absorption correction (transmission factors 0·2974–0·5195) and extinction correction (secondary-extinction value $3·7 \times 10^{-5}$) applied; Cu sited at centre of symmetry; positions of all the non-hydrogen atoms established by means of *AUTOFOUR* (Kinneging & de Graaff, 1984); H atoms located by means of difference Fourier syntheses except for the positions of two H atoms, which were calculated; F used in full-matrix least-squares refinement; non-H atoms refined with anisotropic temperature factors; H atoms refined isotropically; $(\Delta/\sigma)_{\text{max}} \leq 0·046$; $w(F) = 1/\sigma^2(F)$ [$\sigma^2(F)_{\text{rel}} = 0·5 \times \sigma^2(I)_{\text{abs}}$; $\sigma^2(I)_{\text{abs}} = \sigma^2(I)$(counting statistics) + $0·0027I^2$]; maximum absolute excursions in final difference Fourier 0·32 e Å^{-3}, within 0·53 Å of C(2); $R = 0·039$, $wR = 0·044$; $S = 1·334$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations performed on the Leiden University IBM 3083 computer using a local set of programs.

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors are given in Table 1 and bond distances and angles in Table 2.* An *ORTEP* (Johnson, 1965) drawing of the molecular geometry showing the atomic labelling is depicted in Fig. 1, and a drawing of the unit cell showing the hydrogen bonds in Fig. 2. H atoms have been omitted for clarity.

The Cu atom at a symmetry centre is coordinated by two N atoms of two 2-methylbenzimidazole molecules and two O atoms of two formate ions in a square-planar coordination geometry, with Cu—O(1) = 1·985 (1) Å and Cu—N(1) = 1·971 (1) Å. This Cu—N distance is similar to corresponding distances in the structures of known Cu–imidazole compounds: *e.g.* [$Cu(im)_4(I_2)$], 1·98–2·04 Å (Akhtar, Goodgame, Goodgame, Ravner-Canham & Skapski, 1968); [$CuCl_2\{(Me)im\}_2$], 1·962 (4)–1·975 (5) Å (Van Ooijen, Reedijk & Spek, 1979).

The Cu—O distance is typical of Cu—O bond lengths in such complexes, also found in tetra-μ-acetato-bis(benzimidazole)copper(II) (Bukowska-Strzyżewska, Skoweranda & Tosik, 1982) in which the Cu—O(acetato) bond lengths are 1·971 (4)–1·986 (4) Å.

The distance of the semi-coordinating O(2) atoms of the formate group to Cu is 2·668 (1) Å.

The $\nu_{\text{N-H}}$ stretching vibration of the ligand is observed as a very broad band in the 2600–3200 cm^{-1} region, centred at 2900 cm^{-1}, which is indicative of a relatively strong hydrogen-bonding interaction between the non-coordinating N(2) of the ligand and the semi-coordinating O(2) of the formate group of a neigh-

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43160 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bouring molecule. The O(2)···N(1) distance is 2·763 (2) Å, the hydrogen-bond angle N(2)—H···O(2) is 156 (3)°. From the $\nu_{\text{N-H}}$ observed at about 2900 cm^{-1} one would predict (Bellamy & Owen, 1968) an N—H···O distance of 2·71 Å. ($\nu_{\text{obs}} = 580$ cm^{-1} as compared with the $\nu_{\text{N-H}}$ of free 2-methylbenzimidazole at 3484 cm^{-1}.) The difference between the calculated and observed hydrogen-bond lengths may be explained by the fact that the hydrogen bond N(2)—H···O(2) is not linear. There is no stacking of the benzimidazole rings in the crystal.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (× 10^2) *of the non-hydrogen atoms*

$$B_{\text{eq}} = \tfrac{8}{3}\pi^2 \,\text{Tr}\, \text{U}.$$

	x	y	z	B_{eq}(Å^2)
Cu	0	0	0	277 (1)
O(1)	−2191 (2)	240 (1)	949 (1)	391 (3)
O(2)	852 (3)	725 (1)	2299 (1)	495 (4)
N(1)	−228 (2)	1398 (1)	−532 (1)	320 (3)
N(2)*	−1522 (3)	2869 (1)	−1220 (2)	429 (4)
C(1)	−1150 (4)	599 (1)	1965 (2)	430 (6)
C(2)	1418 (3)	2101 (1)	−93 (2)	336 (4)
C(3)	3536 (3)	1990 (2)	637 (2)	448 (5)
C(4)	4767 (5)	2845 (2)	916 (3)	606 (8)
C(5)	3967 (6)	3760 (2)	512 (2)	628 (8)
C(6)	1863 (5)	3887 (2)	−227 (2)	543 (7)
C(7)	585 (3)	3035 (1)	−533 (2)	384 (4)
C(8)	−1945 (3)	1889 (1)	−1205 (2)	362 (4)
C(9)	−4040 (4)	1429 (3)	−1878 (3)	539 (7)

Estimated standard deviations in the least significant digits are given in parentheses.

* The equivalent position of N(2) participating in the O(2)···N(2) hydrogen bond is generated by the symmetry operation x+0·5, −y+0·5, z+0·5.

Table 2. *Bond distances* (Å) *and angles* (°) *with their estimated standard deviations given in parentheses*

Coordination of copper(II)			
Cu—O(1)	1·985 (1)	O(1)—Cu—O(2)	54·2 (1)
Cu—N(1)	1·971 (1)	O(1)—Cu—N(1)	90·0 (1)
Cu—O(2)	2·668 (1)	Cu—O(1)—C(1)	106·0 (1)
		Cu—N(1)—C(8)	129·3 (1)
		Cu—N(1)—C(2)	123·7 (1)
Formate group			
C(1)—O(1)	1·249 (3)	O(1)—C(1)—O(2)	125·4 (2)
C(1)—O(2)	1·234 (3)		
2-Methylbenzimidazole molecule			
C(2)—N(1)	1·397 (2)	N(1)—C(2)—C(7)	108·1 (2)
N(1)—C(8)	1·323 (2)	C(8)—N(1)—C(2)	106·5 (1)
C(8)—C(9)	1·475 (3)	N(1)—C(8)—C(9)	124·8 (2)
C(8)—N(2)	1·350 (3)	N(1)—C(8)—N(2)	111·2 (2)
N(2)—C(7)	1·369 (3)	C(9)—C(8)—N(2)	124·0 (2)
C(7)—C(2)	1·404 (2)	C(8)—N(2)—C(7)	108·7 (2)
C(2)—C(3)	1·380 (3)	N(2)—C(7)—C(2)	105·6 (2)
C(3)—C(4)	1·380 (3)	N(2)—C(7)—C(6)	133·5 (2)
C(4)—C(5)	1·365 (5)	C(7)—C(6)—C(5)	116·7 (2)
C(5)—C(6)	1·378 (4)	C(6)—C(5)—C(4)	121·6 (2)
C(6)—C(7)	1·395 (3)	C(5)—C(4)—C(3)	122·9 (3)
		C(4)—C(3)—C(2)	116·4 (2)
		C(3)—C(2)—C(7)	121·3 (2)
		C(3)—C(2)—N(1)	130·6 (2)

The C—O distances of the formate ion C(1)—O(1) = 1·249 (3) Å and C(1)—O(2) = 1·234 (3) Å are almost identical, which indicates some delocalization of the π electrons between the two C—O bonds. This is in contrast to corresponding bond lengths in [Cu(benzimidazole)$_2$(CHO$_2$)$_2$(H$_2$O)] (Bukowska-Strzyżewska & Tosik, 1983), in which the C—O bond length of the coordinating O, 1·248 (8) Å, is 0·037 Å shorter than the C—O bond length of the non-coordinating O atom.

The 2-methylbenzimidazole ligand is planar within experimental error, with an angle of 7·0 (1)° with respect to the Cu—N(1) bond and an angle of 67·3 (1)° with respect to the plane of the CuN$_2$O$_2$ unit. The dimensions of the imidazole ring in different compounds containing coordinated benzimidazole rings appear to be comparable; *e.g.* [Cu(benzimidazole)$_2$(CH$_3$CO$_2$)$_2$] (Bukowska-Strzyżewska *et al.*, 1982) shows distances corresponding to N(1)—C(8) and N(1)—C(2) which are similar to those in the title compound; in [Cu(benzimidazole)$_2$(HCO$_2$)$_2$(H$_2$O)] (Bukowska-

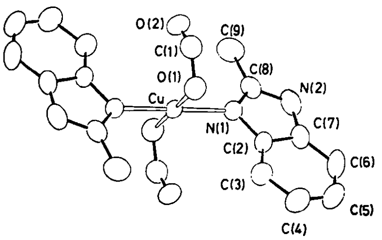

Fig. 1. An *ORTEP* drawing (Johnson, 1965) of the title compound, showing the atomic labelling used. Hydrogen atoms have been omitted for clarity.

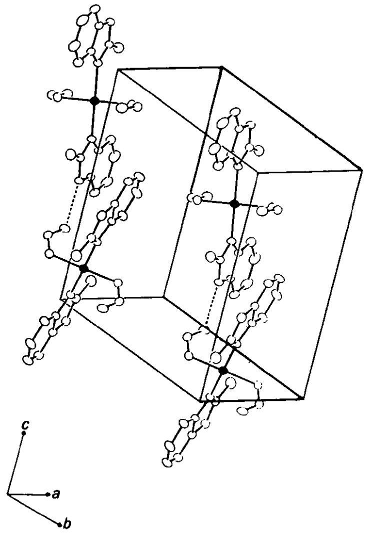

Fig. 2. An *ORTEP* drawing (Johnson, 1965) of the unit cell showing the molecular packing and the hydrogen bonds.

Strzyżewska & Tosik, 1983), the distance corresponding to N(1)—C(8) is 1·31 (1) Å [1·323 (2) Å in the title compound]; however, the distance corresponding to N(1)—C(2) is somewhat longer [1·543 (9) Å compared to 1·397 (2) Å].

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Structure of Diaquatriglutaratodineodymium(III) Dihydrate

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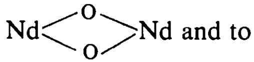
Abstract. [$Nd_2(C_5H_6O_4)_3(H_2O)_2$].$2H_2O$, $M_r = 750{\cdot}84$, monoclinic, $C2/c$, $a = 8{\cdot}061$ (2), $b = 15{\cdot}080$ (3), $c = 19{\cdot}740$ (3) Å, $\beta = 93{\cdot}70$ (4)°, $V = 2394{\cdot}6$ (7) Å^3, $Z = 4$, $D_m = 2{\cdot}10$ (1), $D_x = 2{\cdot}082$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 4{\cdot}38$ mm^{-1}, $F(000) = 1456$, $T = 297$ K, $R = 0{\cdot}033$ for 2525 reflections. Complex possesses twofold (C_2) symmetry. The coordination polyhedron of the Nd ions comprises eight O atoms from glutarate ions and one from a water molecule. Each Nd ion is linked to two Nd ions by oxygen bridges of type  $\mathrm{Nd}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\diamond}}\mathrm{Nd}$ and to six other ones by glutarate ions [$NdOOC(CH_2)_3COONd$], forming a three-dimensional polymeric structure. Nd—O distances are 2·425 (6)–2·665 (6) Å.

Introduction. Recently we have published spectroscopic and crystal structure data for lanthanide complexes with amino acids (Legendziewicz, Huskowska, Strek & Jeżowska-Trzebiatowska, 1981; Legendziewicz, Huskowska, Waskowska & Argay, 1984; Legendziewicz, Huskowska, Argay & Waskowska, 1984; Legendziewicz, Głowiak, Huskowska & Dao-Cong-Ngoan, 1985). From our spectroscopic studies it follows that in the case of dicarboxylic amino acids the mode of bonding with Ln^{III} ions depends upon the chain length of the amino acid molecules. We have now begun a study of the crystal structures of lanthanide compounds with dicarboxylic amino acids (Głowiak, Legendziewicz, Dao-Cong-Ngoan & Huskowska, 1986) and dicarboxylic acid analogues of the respective amino acids. Our goal in the present work was the determination of the coordination mode of the glutaric acid molecule (analogue of glutamic acid) with Nd^{III} and the dependence of the bonding upon the chain length of the carboxylic acid molecule.

The above problems are important since lanthanide ions are widely applied as metal probes in studies of the calcium bonding of proteins and of other biological systems.

Experimental. Rose-coloured crystals obtained from aqueous solution, dimensions 0·25 × 0·3 × 0·4 mm; D_m by flotation in chloroform/ethylene bromide. Space group determination based on Weissenberg photographs; cell parameters by least-squares orientation matrix program using 15 reflections in the range $23 < 2\theta < 30°$. Syntex $P2_1$ diffractometer, graphite monochromator; 2749 unique reflections measured; $2\theta_{\max} = 55{\cdot}0°$; variable θ–2θ scan, scan rate 2·0–

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