

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$\Delta\rho_{\max} = 1.43 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.159$	$\Delta\rho_{\min} = -1.00 \text{ e } \text{\AA}^{-3}$
$S = 1.224$	Extinction correction:
3776 reflections	<i>SHELXL97</i>
173 parameters	Extinction coefficient:
H atoms fixed with an	0.0002 (2)
overall U_{iso}	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + 19.82P]$	<i>International Tables for</i>
where $P = (F_o^2 + 2F_c^2)/3$	<i>Crystallography</i> (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Sn1—C1	2.121 (9)	Sn1—O2'	2.484 (6)
Sn1—C3	2.127 (10)	S1—C7	1.771 (13)
Sn1—C2	2.130 (9)	S1—C8	1.800 (15)
Sn1—O1	2.152 (6)		
C1—Sn1—C3	117.0 (4)	C3—Sn1—O2'	83.9 (3)
C1—Sn1—C2	115.5 (4)	C2—Sn1—O2'	87.9 (3)
C3—Sn1—C2	126.5 (4)	O1—Sn1—O2'	174.4 (2)
C1—Sn1—O1	88.6 (3)	C7—S1—C8	101.1 (7)
C3—Sn1—O1	93.7 (3)	C4—O1—Sn1	122.6 (5)
C2—Sn1—O1	97.6 (3)	C4—O2—Sn1 ^{II}	164.6 (6)
C1—Sn1—O2'	88.0 (3)		

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The space group $P2_1/n$ was determined uniquely from the systematic absences. The final difference map had a peak of $1.43 \text{ e } \text{\AA}^{-3}$ close to the Sn atom (1.4 \AA) and was of no chemical significance.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976) in *TEXSAN*. Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1466). Services for accessing these data are described at the back of the journal.

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Dimeric (pyrazole- N^2)(N -salicylidene-2,2-dimethylglycinato- O, N, O')copper(II) pyrazole solvate

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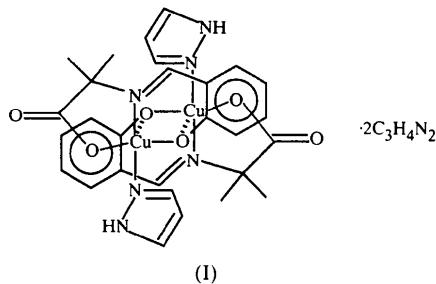
(Received 16 April 1999; accepted 19 May 1999)

Abstract

In the title compound, bis(μ - N -salicylidene-2,2-dimethylglycinato)bis[(pyrazole)copper(II)] bis(pyrazole) solvate, $[\text{Cu}_2(\text{C}_{11}\text{H}_{11}\text{NO}_3)_2(\text{C}_3\text{H}_4\text{N}_2)_2] \cdot 2\text{C}_3\text{H}_4\text{N}_2$, the Cu^{II} atom adopts a square-pyramidal copper(II) coordination with both a tridentate 2,2-dimethyl- N -salicylidene-glycinato Schiff base dianion and a pyrazole ligand forming the basal plane. The apex of the pyramid is occupied by an O atom from an adjacent chelate molecule at a distance of 2.605 (2) \AA , building a centrosymmetric dimer. All copper polyhedra belonging to one dimer are oriented parallel to each other, whereas the dimers are ordered antiferrodistortively.

Comment

Recently, the polymeric structures of pyrazole(*N*-salicylidene-*S*-2-methylglycinato)copper(II) dihydrate and pyrazole(*N*-salicylidene-*rac*-2-methylglycinato)copper(II) pyrazole solvate (Warda *et al.*, 1997) were reported. These compounds form chain structures *via* carboxylic oxygen and crystallize with two water molecules in the *S* form and with one pyrazole molecule in the racemic form. In this paper, we present a very similar complex with 2,2-dimethylglycine instead of 2-methylglycine, namely dimeric pyrazole(*N*-salicylidene-2,2-dimethylglycinato)copper(II) pyrazole solvate, (I).



The Cu^{II} ion has a square-pyramidal (4 + 1) coordination geometry defined by the tridentate *N*-salicylidene-2,2-dimethylglycinato dianion (ONO²⁻ chelator) and one N atom of the neutral pyrazole ligand in the basal plane. The Cu—N and Cu—O bond distances in the equatorial plane [Cu—N 1.925 (2) and 1.972 (2) Å, and Cu—O 1.903 (2) and 1.928 (2) Å; Table 1] do not differ significantly from those of the similar compounds

mentioned above. The Cu atom is displaced from this plane by 0.101 (1) Å toward the apical ligand.

The O1 atom (Fig. 1) is part of the basal plane of one molecule and acts at the same time as the apical ligand to the copper centre of a second monomer at a distance of 2.605 (2) Å, forming a centrosymmetric dimer. In addition, this dimer is connected to non-coordinated pyrazole rings *via* hydrogen bonds. The H31 atom of the coordinated pyrazole ligand has contacts to O2 and to N5 of the non-ligating pyrazole, and is therefore tricoordinated. The non-ligating pyrazole ring is further connected to O3 *via* H41 (see Table 2). The dimeric moieties thus formed are separated in the crystal structure.

The Cu···Cu spacing within the dimers is 3.3588 (4) Å and both Cu atoms are magnetically equivalent. The Cu···Cu($\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$) distance between two differently oriented dimers is 8.4225 (8) Å. This value is higher than the coupling distance of 8.3 Å (Warda, 1997) determined by electron paramagnetic resonance (EPR) spectroscopy for a series of related complexes. Therefore, a molecular *g* tensor is expected and this is indeed found from EPR experiments. The dimers are ordered antiferrodistortively (Fig. 2) with a tilting angle 2γ of 79.3 (2)° (it should be noted that 2γ is different from the cell parameter γ). This is nicely reflected by the phase shift of 80° of the EPR single-crystal measurements. The powder spectrum shows an anisotropic signal superimposed by an isotropic signal. The latter signal can be tentatively assigned as resulting from an electron transition to an *s* orbital of the non-coordinated pyrazole molecule.

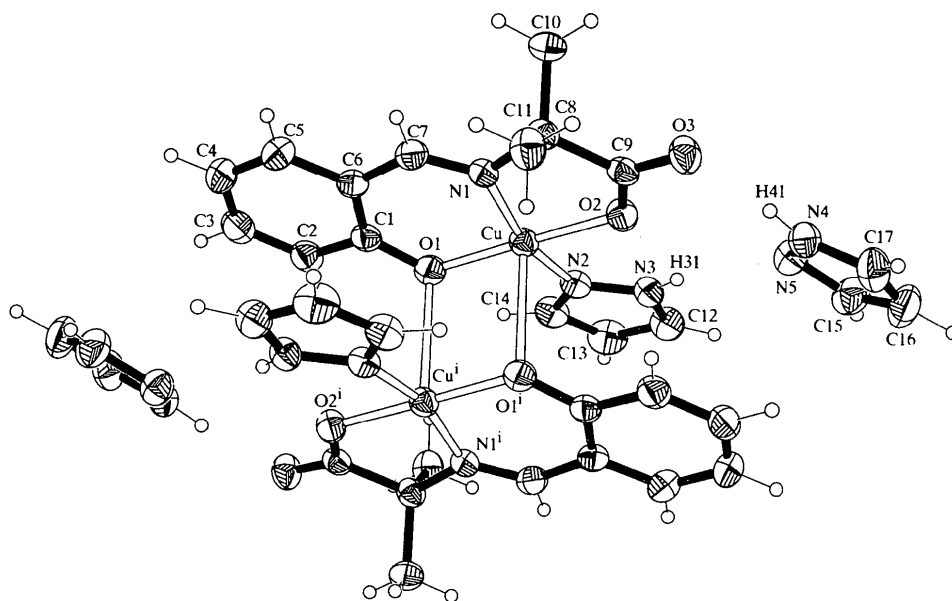


Fig. 1. The title compound in the dimeric form with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

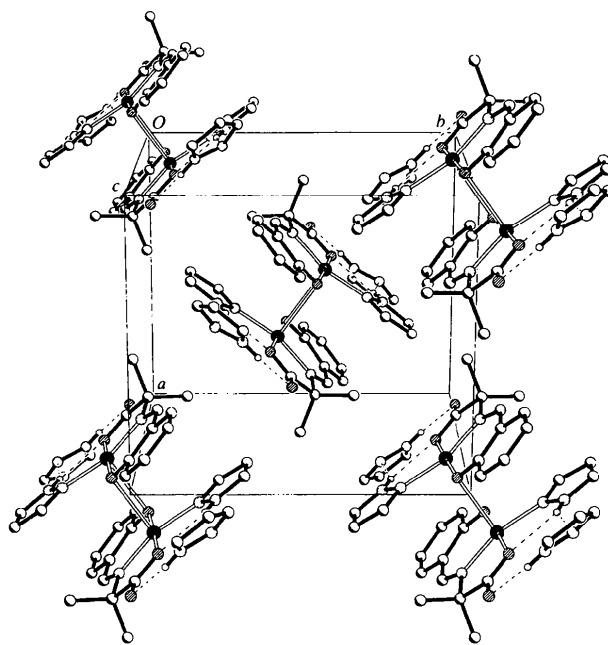


Fig. 2. The packing diagram of the title compound. The non-bridging H atoms have been omitted for clarity.

Experimental

The title compound was synthesized by the reaction of aqua(*N*-salicylidene- α -aminoisobutyrate)copper(II) with pyrazole in ethanol at 343 K. Clear grey-blue plates grew over a period of a few days (Fujimaki *et al.*, 1971; Warda, 1994).

Crystal data

[Cu₂(C₁₁H₁₁NO₃)₂-
(C₃H₄N₂)₂] \cdot 2C₃H₄N₂

$M_r = 809.82$

Monoclinic

$P2_1/n$

$a = 11.4095$ (9) Å

$b = 12.3701$ (6) Å

$c = 13.1335$ (10) Å

$\beta = 92.864$ (9)°

$V = 1851.3$ (2) Å³

$Z = 2$

$D_x = 1.453$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 5000 reflections

$\theta = 2-25^\circ$

$\mu = 1.206$ mm⁻¹

$T = 193$ (2) K

Rectangular plate

$0.46 \times 0.39 \times 0.08$ mm

Grey

Data collection

Stoe IPDS diffractometer

Stoe IPDS image plate scans

Absorption correction:

integration (XPREP in

SHELXTL; Siemens,

1996a)

$T_{\min} = 0.606$, $T_{\max} = 0.913$

13 085 measured reflections

3274 independent reflections

2529 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\text{max}} = 25.03^\circ$

$h = -13 \rightarrow 13$

$k = -13 \rightarrow 14$

$l = -15 \rightarrow 15$

Intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.074$

$S = 0.946$

3274 reflections

241 parameters

H atoms treated by a

mixture of independent

and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.384$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.221$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Cu—O1	1.9031 (16)	Cu—N2	1.9723 (19)
Cu—N1	1.9248 (19)	Cu—O1 ⁱ	2.6050 (16)
Cu—O2	1.9280 (15)		
O1—Cu—N1	95.23 (7)	O2—Cu—N2	88.48 (7)
O1—Cu—O2	178.02 (7)	O1—Cu—O1 ⁱ	84.94 (6)
N1—Cu—O2	83.94 (7)	N1—Cu—O1 ⁱ	103.07 (7)
O1—Cu—N2	92.74 (7)	O2—Cu—O1 ⁱ	93.48 (6)
N1—Cu—N2	164.31 (8)	N2—Cu—O1 ⁱ	91.06 (6)

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

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
N3—H31...O2	0.88 (3)	2.20 (3)	2.763 (3)	117 (3)
N3—H31...N5	0.88 (3)	2.18 (3)	2.959 (3)	147 (3)
N4—H41...O3	0.89 (3)	1.94 (3)	2.831 (3)	174 (3)

All H atoms, except the pyrazole N—H atoms, were included at calculated positions using SHELXL97 (Sheldrick, 1997) and refined using a riding model. The U_{iso} values for H atoms of CH and CH₃ were taken as $1.2U_{\text{eq}}$ and $1.5U_{\text{eq}}$ of the parent atoms, respectively. The H31 and H41 atoms were found from difference Fourier syntheses and refined with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the carrier N atoms; N—H distances were restrained to be equal.

Data collection: EXPOSE (Stoe & Cie, 1997a). Cell refinement: CELL (Stoe & Cie, 1997b). Data reduction: INTEGRATE (Stoe & Cie, 1997c). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97. Molecular graphics: XP in SHELXTL (Siemens, 1996b). Software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1292). Services for accessing these data are described at the back of the journal.

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Bis[2-(2-ethoxyethyl)-*N,N,N',N'*-tetraethylmalondiamide-*O*¹,*O*³]tris(nitrato-*O,O'*)-lanthanum(III)

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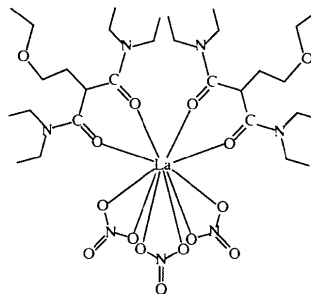
Abstract

2-(2-Ethoxyethyl)-*N,N,N',N'*-tetraethylmalondiamide (TEEEMA, C₁₅H₃₀N₂O₃) reacts with lanthanum(III) nitrate to give the title complex, [La(NO₃)₃(TEEEMA)₂], in which the two carboxyl functions of each TEEEMA ligand are bonded to the metal ion together with three bidentate nitrate ions. This structure establishes that the ether O atom of the central chain of TEEEMA is not bonded to the metal ion, at least in the solid state. The coordination environment geometry is different from that of the lanthanum complex of *N,N,N',N'*-tetraethylmalondiamide (TEMA).

Comment

In the course of studies related to nuclear fuel reprocessing, malondiamides have been proposed as extractants able to separate actinides(III) from the majority of fission products, with the exception of lanthanides(III) which are co-extracted with actinides(III) (Cuillerdier *et al.*, 1991). Extensive data have been compiled so as to understand the extraction mechanisms (Nigond, 1992; Nigond *et al.*, 1994; Madic & Hudson, 1998). The first step in such investigations is the determination of the nature of the complex species which are formed (stoichiometry, structure and nature of bonding). The optimization of a suitable extractant for this process

was undertaken and a large number of molecules with the general formula *RR'N—CO—CHR''—CO—NRR'* was evaluated (Madic & Hudson, 1998). Malondiamides with *R''* = C₂H₄OC_nH_{2n+1} are molecules of interest because they lead to higher extraction of both actinides(III) and lanthanides(III). In order to explain this behaviour, the participation in complexation of the ether O atom present in the *R''* radical was suggested, but no structural evidence was available. The present study of the title complex, (I), deals with a ligand which belongs to this family and contributes to the elucidation of the last point.



(I)

Some crystal structures of complexes formed by malondiamide derivatives, *e.g.* *N,N,N',N'*-tetramethyl-, *N,N,N',N'*-tetraethyl-, *N,N'*-dicyclohexyl-*N,N'*-dimethyl- and *N,N'*-dimethyl-*N,N'*-diphenylmalondiamide, with lanthanides (La³⁺, Nd³⁺, Sm³⁺, Er³⁺ and Yb³⁺) have been determined (Castellano & Becker, 1981; Byers *et al.*, 1994; Chan *et al.*, 1997; Den Auwer *et al.*, 1999). The malondiamide/metal ion stoichiometry of the complexes formed is 1:1 or 2:1 when the three counter-ions are bonding (NO₃⁻), whereas it is 4:1 or even 5:1 when the counter-ions are non-bonding (PF₆⁻). In most cases, the malondiamide is bidentate, so that the metal ion coordination number is between 8 and 10. Some solid-state and solution EXAFS (Extended X-ray Absorption Fine Structure) measurements have also been performed recently (Den Auwer *et al.*, 1999). In the case of the La³⁺ complex of *N,N,N',N'*-tetraethylmalondiamide (TEMA), the two ligands are roughly coplanar, two nitrate ions being located on each side and the third one crossing this plane (Byers *et al.*, 1994). The present ligand, TEEEMA, differs from TEMA by the presence of a -(CH₂)₂-O-CH₂CH₃ ether chain on the central methylenic C atom. The complex formed with La³⁺ has the same 2:1 stoichiometry as the TEMA complex, with three bidentate nitrate ions. The ether O atoms are not bonded to the metal ion, the ether chains being stretched away from the complex core. The La—O_{TEEEMA} distances [mean value 2.52 (2) Å], as well as the La—O_{nitrate} distances [mean value 2.64 (3) Å], are in agreement with those already found [mean values 2.53 (5) and 2.70 (8) Å, respectively]. However, the