

$\omega$  scan  
Absorption correction:  
 $\psi$  scan (North *et al.*,  
1968)  
 $T_{min} = 0.729$ ,  $T_{max} = 0.822$   
10 063 measured reflections  
4724 independent reflections

$R_{int} = 0.024$   
 $\theta_{max} = 25.69^\circ$   
 $h = -10 \rightarrow 10$   
 $k = 0 \rightarrow 18$   
 $l = -22 \rightarrow 22$   
3 standard reflections  
frequency: 60 min  
intensity decay: 1%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.028$   
 $wR(F^2) = 0.072$   
 $S = 1.002$   
4724 reflections  
349 parameters  
H atoms: see text  
 $w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 1.1434P]$   
where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.846 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{min} = -0.402 \text{ e } \text{\AA}^{-3}$   
Extinction correction: none  
Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

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

Sn1—C1	2.114 (3)	Sn1—O1'	2.939 (2)
Sn1—C5	2.112 (3)	Sn1—O3	2.125 (2)
Sn1—N1	2.198 (2)	Sn1—O6	2.409 (2)
Sn1—O1	2.299 (2)		
C1—Sn1—C5	156.6 (1)	N1—Sn1—O1	69.2 (1)
C1—Sn1—N1	100.8 (1)	N1—Sn1—O1'	136.1 (1)
C1—Sn1—O1	86.3 (1)	N1—Sn1—O6	152.4 (1)
C1—Sn1—O1'	78.1 (1)	N1—Sn1—O3	72.0 (1)
C1—Sn1—O3	101.8 (1)	O1—Sn1—O1'	66.9 (1)
C1—Sn1—O6	83.1 (1)	O1—Sn1—O3	141.2 (1)
C5—Sn1—N1	99.2 (1)	O1—Sn1—O6	138.4 (1)
C5—Sn1—O1	89.4 (1)	O1'—Sn1—O3	151.8 (1)
C5—Sn1—O1'	79.0 (1)	O1'—Sn1—O6	71.5 (1)
C5—Sn1—O3	95.9 (1)	O3—Sn1—O6	80.4 (1)
C5—Sn1—O6	84.9 (1)		

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

A riding model was used to refine the H atoms, with  $U(H) = 1.5U_{eq}(C)$ . The water H atoms were located and refined with  $U = 0.05 \text{ \AA}^2$ . The pyridinium H atom is disordered between the N3 and N4 atoms, and was refined as one H atom with  $U = 0.05 \text{ \AA}^2$ .

Data collection: *CAD-4/PC* (Kretschmar, 1994). Cell refinement: *CELDIM* in *CAD-4 VAX/PC* (Enraf-Nonius, 1988). Data reduction: *XCAD4* (Harms, 1997). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1200). Services for accessing these data are described at the back of the journal.

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## Bis(3,5-dimethylpyrazole-*N*<sup>2</sup>)(2,2-dimethyl-*N*-salicylidene-glycinato-*O,N,O'*)copper(II)

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### Abstract

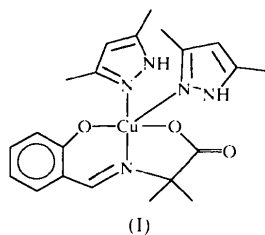
In the title compound,  $[Cu(C_{11}H_{11}NO_3)(C_5H_8N_2)_2]$ , the  $Cu^{II}$  atom adopts a square-pyramidal coordination, with a tridentate 2,2-dimethyl-*N*-salicylidene-glycinate Schiff base dianion and a 3,5-dimethylpyrazole ligand bound in the basal plane. The apex of the elongated pyramid is occupied by a second 3,5-dimethylpyrazole molecule, with a Cu—N distance of 2.461 (2) Å. All molecules are arranged in a single magnetic orientation.

### Comment

Owing to the diversity of resulting structures, copper(II) complexes with tridentate Schiff base dianions of the *N*-salicylideneaminoacidato type ( $TSB^{2-}$ ) present a suitable model for the elucidation of structural and spectroscopic correlations. We are interested in the effect of the copper coordination, the Jahn–Teller distortion

and dipolar interactions between different polyhedra on the electron paramagnetic resonance (EPR) spectra. For an unambiguous interpretation of EPR results, X-ray structure determinations of a series of compounds were undertaken.

The structure of bis(3,5-dimethylpyrazole)(*N*-salicylidene-glycinato)copper(II) (Warda, 1997) was reported recently, in which the achiral C8 atom bears two H atoms. In the present communication, we report on the effect of two methyl groups at C8 in the closely related structure bis(3,5-dimethylpyrazole)(2,2-dimethyl-*N*-salicylidene-glycinato)copper(II), (I). The Cu atoms



have a [4+1] square-pyramidal coordination geometry, with three donor atoms of the tridentate (TSB) 2,2-dimethyl-*N*-salicylidene-glycinato dianion ( $\text{ONO}^{2-}$  chelator) and one N atom of a 3,5-dimethylpyrazole ligand in the basal plane (Fig. 1).

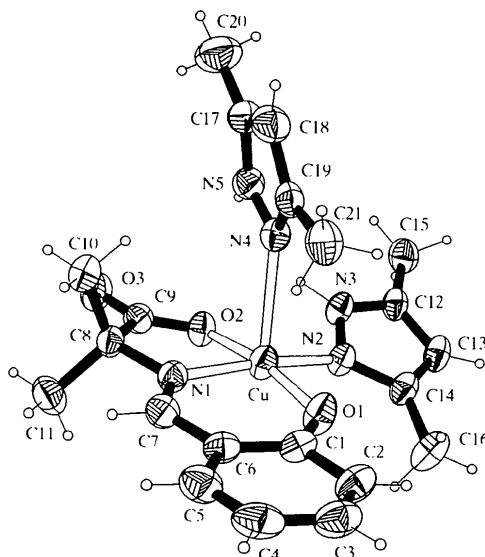


Fig. 1. The asymmetric unit of the title compound with the atomic numbering scheme. Ellipsoids are drawn at the 40% probability level.

The apical coordination site is occupied by an N-donor atom of the second coordinated 3,5-dimethylpyrazole ligand at an apical Cu—N4 distance of 2.461 (2) Å. The Cu atom is displaced from the basal plane by 0.164 (1) Å towards the apical ligand.

The equatorially coordinated pyrazole ligand is twisted with respect to the basal plane (O1, O2, N1, N2) by 26.6 (1)° and the apical ligand is twisted by 75.1 (1)°. Intermolecular hydrogen bonding across an inversion centre leads to a dimeric association [N3—H31...O3<sup>i</sup> and N5—H51...O3<sup>i</sup>; symmetry code: (i) 1 - x, 2 - y, 2 - z]. There is also an interaction between atoms H31 and O2 (Table 2) within the molecule.

The small yet non-negligible shortening of the equatorial copper distances when going from the C8-dihydro (Warda, 1997) to the C8-dimethyl compound (see Table 1) is closely related to the positive inductive effect of the methyl groups increasing the donor ability of the attached ligand atoms. It is interesting to note that the strengthening of the equatorial bonds is accompanied with a significant weakening of the apical Cu—N bonds, as is seen by a comparison of the corresponding Cu—N bond lengths [2.461 (2) Å for the C8-dimethyl compound *versus* 2.342 (3) Å for the C8-dihydro compound (Warda, 1997)].

Obviously, the capacity for copper bonding is essentially constant and is redistributed between equatorial and apical distances, as is reflected by the average metal–ligand bond lengths [2.042 (3) Å for the C8-dihydro compound and 2.053 (2) Å for the title compound].

The difference between the equatorial and apical bond lengths is also reflected by the EPR spectra, which show that the averaged *g* tensor is significantly lowered for the title compound compared with the C8-dihydro compound (Warda, 1994, 1997).

## Experimental

The title compound was synthesized from aqua(2,2-dimethyl-*N*-salicylidene-glycinato)copper(II) and 3,5-dimethylpyrazole in ethanol at 333 K. Dark-green crystals grew within a few days (Fujimaki *et al.*, 1971; Warda, 1994).

### Crystal data

[Cu(C<sub>11</sub>H<sub>11</sub>NO<sub>3</sub>)(C<sub>5</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]

*M<sub>r</sub>* = 461.02

Triclinic

*P* $\bar{1}$

*a* = 9.4468 (9) Å

*b* = 10.7321 (8) Å

*c* = 10.9452 (9) Å

$\alpha$  = 91.601 (8)°

$\beta$  = 93.036 (9)°

$\gamma$  = 92.609 (9)°

*V* = 1106.45 (16) Å<sup>3</sup>

*Z* = 2

*D<sub>r</sub>* = 1.384 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Mo *K*α radiation

$\lambda$  = 0.71073 Å

Cell parameters from 5000 reflections

$\theta$  = 2.16–25.93°

$\mu$  = 1.018 mm<sup>-1</sup>

*T* = 293 (2) K

Prism

0.30 × 0.20 × 0.10 mm

Dark green

### Data collection

Stoe IPDS diffractometer

Image plate scans

2641 reflections with

*I* > 2σ(*I*)

Absorption correction:  
by integration (Siemens,  
1996a)  
 $T_{\min} = 0.750$ ,  $T_{\max} = 0.905$   
11 014 measured reflections  
4038 independent reflections

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.059$   
 $S = 0.995$   
4038 reflections  
282 parameters  
H atoms: see below  
 $w = 1/[\sigma^2(F_o^2) + (0.0153P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$R_{\text{int}} = 0.043$   
 $\theta_{\max} = 25.93^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -13 \rightarrow 13$   
 $l = -13 \rightarrow 13$

$\Delta\rho_{\max} = 0.228 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.201 \text{ e } \text{\AA}^{-3}$

Extinction correction:  
*SHELXL97*

Extinction coefficient:  
0.0105 (5)

Scattering factors from  
*International Tables for  
Crystallography* (Vol. C)

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

Cu—O1	1.8994 (16)	Cu—N2	2.004 (2)
Cu—N1	1.938 (2)	Cu—N4	2.461 (2)
Cu—O2	1.9624 (15)		
O1—Cu—N1	92.86 (8)	O2—Cu—N2	89.35 (8)
O1—Cu—O2	169.81 (8)	O1—Cu—N4	101.52 (7)
N1—Cu—O2	83.21 (8)	N1—Cu—N4	93.37 (7)
O1—Cu—N2	92.95 (8)	O2—Cu—N4	88.14 (6)
N1—Cu—N2	168.28 (7)	N2—Cu—N4	95.43 (7)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
N3—H31...O2	0.92 (1)	2.39 (1)	2.876 (3)	113 (1)
N3—H31...O3 <sup>i</sup>	0.92 (1)	2.15 (1)	3.027 (3)	159 (1)
N5—H51...O3 <sup>i</sup>	0.91 (1)	1.91 (1)	2.776 (3)	159 (1)

Symmetry code: (i)  $1 - x, 2 - y, 2 - z$ .

All H atoms except those on N atoms were included at calculated positions using *SHELXL97* (Sheldrick, 1997) and refined using a riding model. The  $U_{\text{iso}}$  values for the H atoms of CH and NH groups, and of the methyl groups were taken as  $1.2U_{\text{eq}}$  and  $1.5U_{\text{eq}}$ , respectively, of the carrier atoms. The methyl groups of the pyrazole ligands were refined as rigid groups. The H31 and H51 atoms were found from difference Fourier syntheses and N—H distances were restrained to be equal. The analytical absorption correction based on face-indexing was carried out with the following faces and distances (mm):  $\bar{1}00$  0.0385,  $100$  0.0847,  $01\bar{1}$  0.1347,  $0\bar{1}1$  0.1540,  $121$  0.0770,  $112$  0.0847,  $\bar{1}2\bar{1}$  0.1193 and  $1\bar{1}2$  0.1540.

Data collection: *EXPOSE* (Stoe, 1997a). Cell refinement: *CELL* (Stoe, 1997b). Data reduction: *INTEGRATE* (Stoe, 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: JZ1275). Services for accessing these data are described at the back of the journal.

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### Bis( $\mu$ -3,4-dimethylphosphol-1-yl)bis(tetra-carbonylmanganese)

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#### Abstract

In the title compound,  $[\text{Mn}_2(\text{C}_6\text{H}_8\text{P})_2(\text{CO})_8]$ , the  $\mu_2$ -bridging 3,4-dimethylphosphol-1-yl ligands show distinct localization of the C=C double bonds. The central  $\text{Mn}_2\text{P}_2$  ring fragment is planar, with Mn—P bond lengths of 2.3586 (8)  $\text{\AA}$ .

#### Comment

The phospholyl ring ligand (phosphacyclopentadienyl) and its derivatives, e.g. 3,4-dimethylphospholyl, are well known to form various transition metal complexes and the ability of the ligand to act as different electron donors in different environments has been discussed thoroughly (Abel & Towers, 1979; Mathey *et al.*, 1983). In connection with our interest in bis(phosphido)-bridged transition metal carbonyl complexes (Flörke & Haupt, 1994, 1997), we investigated the structure of the title compound, (I). Only a few examples of complexes containing two phospholyl rings as three-electron bridging ligands are known. These include  $(\mu\text{-L}')_2\text{M}_2(\text{CO})_8$ ,