O1	0.8455 (5)	0.5395 (4)	0.1983 (5)	0.0544 (13)
C7	0.9908 (8)	0.5693 (7)	0.1927 (9)	0.079 (3)
B1	0.3250 (3)	0.3528 (3)	0.1959 (3)	0.055 (2)
F1	0.2085 (4)	0.3438 (4)	0.1061 (4)	0.114 (2)
F2	0.4454 (3)	0.3430 (4)	0.1412 (4)	0.086 (2)
F3	0.3215 (5)	0.2811 (4)	0.2858 (4)	0.126 (2)
F4	0.3236 (5)	0.4436 (3)	0.2524 (5)	0.129 (2)

Table 2. *Selected geometric parameters (Å, °)*

Fe1—C3*A*	1.812 (8)	C1—C2	1.399 (9)
Fe1—C2*A*	1.812 (8)	C1—C6	1.425 (9)
Fe1—C1*A*	1.824 (8)	C2—C3	1.500 (9)
Fe1—C5	2.095 (7)	C3—C4	1.502 (10)
Fe1—C6	2.112 (7)	C4—C5	1.367 (11)
Fe1—C4	2.163 (7)	C5—C6	1.408 (10)
Fe1—C2	2.189 (6)	O1—C7	1.429 (8)
Fe1—C1	2.191 (6)	B1—F1	1.343 (2)
C1*A*—O1*A*	1.129 (8)	B1—F2	1.343 (2)
C2*A*—O2*A*	1.129 (8)	B1—F3	1.344 (2)
C3*A*—O3*A*	1.133 (8)	B1—F4	1.344 (2)
C1—O1	1.336 (8)		
C3*A*—Fe1—C2*A*	97.0 (3)	O2*A*—C2*A*—Fe1	179.2 (6)
C3*A*—Fe1—C1*A*	90.9 (3)	O3*A*—C3*A*—Fe1	178.0 (6)
C2*A*—Fe1—C1*A*	96.2 (3)	O1—C1—C2	124.9 (6)
C3*A*—Fe1—C5	138.4 (3)	O1—C1—C6	115.3 (6)
C2*A*—Fe1—C5	124.5 (3)	C2—C1—C6	119.0 (7)
C1*A*—Fe1—C5	87.6 (3)	O1—C1—Fe1	124.4 (5)
C3*A*—Fe1—C6	101.8 (3)	C2—C1—Fe1	71.3 (4)
C2*A*—Fe1—C6	152.4 (3)	C6—C1—Fe1	67.7 (4)
C1*A*—Fe1—C6	103.4 (3)	C1—C2—C3	118.4 (6)
C5—Fe1—C6	39.1 (3)	C1—C2—Fe1	71.4 (4)
C3*A*—Fe1—C4	165.5 (3)	C3—C2—Fe1	91.9 (4)
C2*A*—Fe1—C4	88.4 (3)	C4—C3—C2	103.9 (6)
C1*A*—Fe1—C4	101.9 (3)	C5—C4—C3	119.7 (7)
C5—Fe1—C4	37.4 (3)	C5—C4—Fe1	68.6 (4)
C6—Fe1—C4	68.8 (3)	C3—C4—Fe1	92.8 (5)
C3*A*—Fe1—C2	100.8 (3)	C4—C5—C6	121.1 (7)
C2*A*—Fe1—C2	88.0 (3)	C4—C5—Fe1	74.0 (5)
C1*A*—Fe1—C2	167.0 (3)	C6—C5—Fe1	71.1 (4)
C5—Fe1—C2	80.0 (3)	C5—C6—C1	117.5 (7)
C6—Fe1—C2	68.9 (3)	C5—C6—Fe1	69.8 (4)
C4—Fe1—C2	65.8 (3)	C1—C6—Fe1	73.7 (4)
C3*A*—Fe1—C1	86.7 (3)	C1—O1—C7	118.1 (6)
C2*A*—Fe1—C1	124.1 (3)	F1—B1—F2	110.0 (2)
C1*A*—Fe1—C1	139.6 (3)	F1—B1—F3	109.3 (2)
C5—Fe1—C1	68.8 (3)	F2—B1—F3	109.7 (2)
C6—Fe1—C1	38.6 (2)	F1—B1—F4	109.3 (2)
C4—Fe1—C1	79.1 (3)	F2—B1—F4	109.7 (2)
C2—Fe1—C1	37.3 (2)	F3—B1—F4	108.8 (2)
O1*A*—C1*A*—Fe1	179.5 (7)		

The geometry of the BF_4 anion was restrained to tetrahedral symmetry, with B—F 1.342 (2) and F—F 2.192 (3) Å. Orientational disorder of the BF_4 anion, evident from excess electron-density maps, required either acceptance of a highly non-realistic molecular geometry or the above restraint. No model involving split molecular positions was obvious and the remaining excess electron density is probably responsible for the relatively high agreement indices. No absorption correction was attempted due to degradation of the crystal after data collection.

Data collection: *XSCANS*2.0 (Siemens, 1992). Cell refinement: *XSCANS*2.0. Data reduction: *XSCANS*2.0. Program(s) used to solve structure: *XS* (Siemens, 1994). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *INSIGHT*II (Biosym/MSI, 1995). Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1242). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Dinuclear Molybdenum Complex: $[\{MoClO(pyridine)_2\}_2(\mu\text{-}S)_2].2C_5H_5N$

Jun Mizutani, Hideo Imoto and Taro Saito

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo, Tokyo 113, Japan. E-mail: taro@chem.s.u-tokyo.ac.jp

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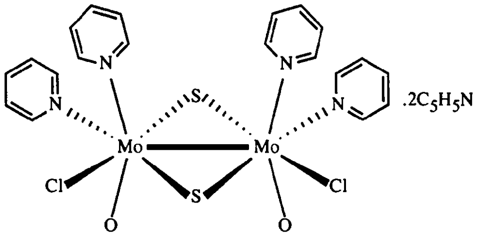
Abstract

In the title dinuclear molybdenum–chloro–oxo–sulfido–pyridine complex, di-μ-sulfido-bis[chloro(oxo)bis(pyridine-*N*)molybdenum](*Mo—Mo*) bis(pyridine) solvate, $[Mo_2Cl_2(O)_2(S)_2(C_5H_5N)_4].2C_5H_5N$, the two Mo atoms are each coordinated by one chloro, one oxo and two pyridine ligands, and are bridged by two μ-S ligands. The distance between the Mo atoms is 2.837 (1) Å, suggesting the existence of an Mo—Mo single bond.

Comment

Excision reactions of non-molecular compounds to extract dinuclear or cluster cores as molecular complexes have been extensively studied, especially with group 6 metal halides/chalcogenides (Lee & Holm, 1990). As examples, we have reported the excision reaction of a molybdenum–chloride–sulfide complex, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Cl_2Cl_{4/2}]_n$, containing a trinuclear cluster core, using triethylphosphine (Saito, Yamamoto, Yamagata & Imoto, 1987) and pyridine/triphenylphosphine (Mizutani, Imoto & Saito, 1994) to give trinuclear cluster complexes containing an $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ core. In the present study, we examined the excision reaction of another molybdenum–chloride–sulfide complex, $Mo_2S_4Cl_6$ $\{[Mo_2(\mu\text{-}S_2)_2Cl_4Cl_{4/2}]_n$; Fedorov, Fedin & Kuz'mina, 1986; Marcoll, Rabenau, Mootz & Wunderlich, 1974$\}$, with pyridine and obtained a new dinuclear molybdenum–chloro–oxo–sulfido complex with pyridine (py) ligands, $[\{MoClO(C_5H_5N)_2\}_2(\mu\text{-}S)_2].2C_5H_5N$, (I).



(I)

The title complex contains two Mo atoms each coordinated by one chloro, one oxo and two pyridine ligands. The pyridine ligands have a *cis* configuration. All the bond distances between molybdenum and the ligands fall into normal ranges. The two $MoClO(py)_2$ moieties are bridged by two μ-S ligands to afford an Mo_2S_2 core. The coordination geometry of molybdenum is distorted octahedral and the two octahedra share one edge formed by two μ-S ligands.

The interatomic distance between the Mo atoms is 2.837 (1) Å, which is in the range of single Mo—Mo bonds (Garner, 1987; Cotton & Walton, 1993). The formal oxidation state of molybdenum is +5 and the total number of *d* electrons is two, which leads to the formation of a single metal–metal bond according to the 18-electron formalism.

The distances between the Mo and O atoms are 1.701 (5) and 1.687 (5) Å, which shows the O atoms to be oxo ligands, rather than aqua or hydroxy ligands (Garner & Charnock, 1987). The oxo ligands coordinate in a *syn* fashion, which is relatively common for dinuclear molybdenum–sulfido complexes having two oxo ligands (Shibahara, 1993).

The title complex is generated by the excision reaction of the non-molecular molybdenum–chloride–sulfide, $Mo_2S_4Cl_6$, with pyridine. The following examples of excision reactions of the same chloride–sulfide have been reported so far: the preparation of $[Mo_2(\mu\text{-}S_2)_2Cl_8]^{2-}$ by $(R_4P)Cl$ (Fenske, Czeska, Schumacher, Schmidt & Dehnicke, 1985) and that of $[Mo_2(\mu\text{-}S_2)_2(S_2)_4]^{2-}$ by $(NH_4)_2S_x$ (Fedin, Geras'ko, Mironov & Fedorov, 1988). In both cases, the $Mo_2(\mu\text{-}S_2)_2$ core structure in the chloride–sulfide is preserved during the excision process. The present complex, however, has an $Mo_2(\mu\text{-}S)_2$ core generated by the loss of one S atom from each S_2 ligand. Although the details of the reaction process are unclear, the loss of sulfur must be due to pyridine being used as a reactant.

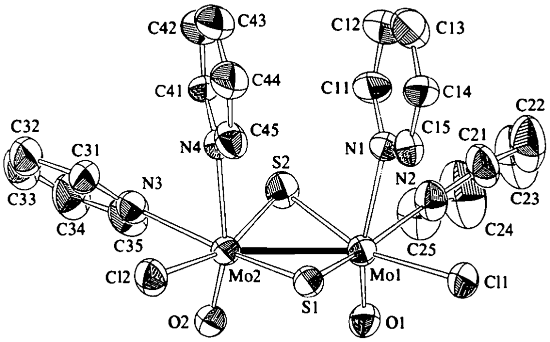


Fig. 1. The molecular structure of (I) shown with 50% probability ellipsoids and without the pyridine solvent molecules.

Experimental

The treatment of 0.1 g of $Mo_2S_4Cl_6$ in 5 ml of pyridine for 30 min at room temperature, with the mixture open to the atmosphere, afforded a clear orange solution. Addition of 1 ml of hexane to the resulting solution gave orange column-shaped single crystals of the title compound after 3 d at room temperature (yield 45%).

Crystal data

$[Mo_2Cl_2(O)_2(S)_2(C_5H_5N)_4]$.-
$2C_5H_5N$
$M_r = 833.5$
Monoclinic
$P2_1/c$
$a = 9.217 (3)$ Å
$b = 24.675 (5)$ Å
$c = 15.698 (4)$ Å
$\beta = 102.89 (2)°$
$V = 3480.2 (15)$ Å^3
$Z = 4$
$D_x = 1.591$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 13–15°$
$\mu = 1.031$ mm^{-1}
$T = 300$ K
Column
$0.3 \times 0.1 \times 0.1$ mm
Orange

Data collection

Rigaku AFC-5*R* diffractometer
$2\theta-\omega$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.85$, $T_{max} = 0.90$
8607 measured reflections
7924 independent reflections

4540 observed reflections $[F > 5\sigma(F)]$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 32$
$l = 0 \rightarrow 20$
3 standard reflections monitored every 150 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.0633$
$wR = 0.0384$
$S = 2.65$
4540 reflections
361 parameters
H atoms not included
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 1.60$ e Å^{-3}
(near Cl1)
$\Delta\rho_{\min} = -1.24$ e Å^{-3}
(near Mo2)
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mo1	0.20453 (9)	0.51972 (2)	0.24463 (4)	0.0420 (4)
Mo2	0.11417 (8)	0.62068 (2)	0.16346 (4)	0.0400 (4)
S1	0.1531 (2)	0.54023 (7)	0.09718 (13)	0.0437 (12)
S2	0.0913 (2)	0.59109 (8)	0.30043 (13)	0.0526 (13)
Cl1	0.2630 (2)	0.42726 (7)	0.20160 (14)	0.0564 (13)
Cl2	0.0476 (2)	0.65848 (8)	0.01475 (13)	0.0575 (14)
O1	0.3876 (6)	0.5352 (2)	0.2818 (3)	0.049 (3)
O2	0.2845 (6)	0.64933 (18)	0.1881 (3)	0.050 (3)
N1	−0.0476 (7)	0.4777 (2)	0.2138 (4)	0.048 (4)
N2	0.2059 (9)	0.4793 (3)	0.3772 (4)	0.059 (4)
N3	0.0232 (9)	0.7033 (2)	0.2021 (4)	0.053 (4)
N4	−0.1541 (7)	0.6041 (2)	0.1270 (4)	0.048 (4)
C11	−0.1469 (11)	0.4897 (3)	0.2635 (5)	0.066 (6)
C12	−0.2916 (12)	0.4669 (3)	0.2452 (6)	0.072 (6)
C13	−0.3345 (11)	0.4298 (3)	0.1744 (6)	0.072 (6)
C14	−0.2284 (10)	0.4191 (3)	0.1244 (5)	0.059 (5)
C15	−0.0881 (10)	0.4429 (3)	0.1453 (5)	0.045 (5)
C21	0.1449 (13)	0.4306 (3)	0.3852 (6)	0.083 (7)
C22	0.1679 (16)	0.4055 (4)	0.4692 (7)	0.104 (9)
C23	0.2483 (18)	0.4322 (4)	0.5422 (7)	0.117 (10)
C24	0.3135 (18)	0.4829 (5)	0.5323 (6)	0.129 (11)
C25	0.2832 (13)	0.5058 (4)	0.4468 (6)	0.086 (7)
C31	−0.0932 (11)	0.7297 (3)	0.1506 (6)	0.061 (6)
C32	−0.1375 (13)	0.7817 (4)	0.1723 (8)	0.084 (8)
C33	−0.0559 (17)	0.8032 (4)	0.2513 (9)	0.096 (9)
C34	0.0614 (15)	0.7759 (4)	0.3053 (7)	0.083 (8)
C35	0.1005 (11)	0.7245 (3)	0.2796 (6)	0.066 (6)
C41	−0.2426 (10)	0.6192 (3)	0.1820 (5)	0.055 (5)
C42	−0.3931 (13)	0.6086 (4)	0.1643 (7)	0.076 (7)
C43	−0.4582 (12)	0.5804 (4)	0.0862 (8)	0.085 (8)
C44	−0.3678 (12)	0.5643 (3)	0.0292 (6)	0.077 (7)
C45	−0.2161 (11)	0.5765 (3)	0.0511 (5)	0.055 (5)
N5†	0.546 (2)	0.3701 (11)	0.3749 (18)	0.086 (7)
C51†	0.663 (5)	0.3801 (16)	0.447 (2)	0.086 (11)
C52†	0.535 (4)	0.3197 (19)	0.325 (2)	0.101 (14)
C53†	0.658 (5)	0.2912 (14)	0.346 (2)	0.105 (12)
C54†	0.792 (3)	0.3003 (14)	0.429 (2)	0.078 (8)
C55†	0.779 (4)	0.3514 (17)	0.469 (2)	0.086 (10)
N6	0.3510 (18)	0.1914 (5)	0.1317 (8)	0.174 (5)
C61	0.275 (2)	0.2365 (8)	0.1164 (10)	0.173 (6)
C62	0.322 (2)	0.2835 (6)	0.0893 (9)	0.153 (5)
C63	0.446 (2)	0.2847 (6)	0.0625 (10)	0.167 (6)
C64	0.5336 (19)	0.2360 (7)	0.0688 (9)	0.166 (6)
C65	0.4860 (19)	0.1926 (6)	0.1087 (9)	0.143 (5)
N7†	0.724 (3)	0.2772 (8)	0.3978 (19)	0.089 (7)
C71†	0.550 (5)	0.339 (2)	0.343 (3)	0.132 (19)
C72†	0.616 (6)	0.3790 (18)	0.414 (3)	0.111 (15)
C73†	0.733 (6)	0.3714 (18)	0.445 (3)	0.120 (17)
C74†	0.802 (4)	0.320 (2)	0.460 (2)	0.123 (15)
C75†	0.594 (5)	0.2855 (16)	0.351 (2)	0.122 (14)

† Site occupancy = 0.5.

Table 2. *Selected geometric parameters (Å, °)*

Mo1—Mo2	2.837 (1)	Mo2—S1	2.306 (2)
Mo1—S1	2.313 (2)	Mo2—S2	2.325 (2)
Mo1—S2	2.317 (2)	Mo2—Cl2	2.461 (2)
Mo1—Cl1	2.473 (2)	Mo2—O2	1.687 (5)
Mo1—O1	1.701 (5)	Mo2—N3	2.335 (7)
Mo1—N1	2.492 (7)	Mo2—N4	2.445 (7)
Mo1—N2	2.305 (7)		
S1—Mo1—S2	101.71 (8)	S1—Mo2—Cl2	85.94 (7)
S1—Mo1—Cl1	86.39 (7)	S1—Mo2—O2	103.5 (2)
S1—Mo1—O1	105.1 (2)	S1—Mo2—N3	165.8 (2)
S1—Mo1—N1	85.58 (15)	S1—Mo2—N4	90.0 (2)
S1—Mo1—N2	163.1 (2)	S2—Mo2—Cl2	160.32 (8)
S2—Mo1—Cl1	161.58 (8)	S2—Mo2—O2	101.1 (2)
S2—Mo1—O1	101.3 (2)	S2—Mo2—N3	85.5 (2)
S2—Mo1—N1	84.8 (2)	S2—Mo2—N4	82.4 (2)
S2—Mo1—N2	84.2 (2)	Cl2—Mo2—O2	94.6 (2)
Cl1—Mo1—O1	92.3 (2)	Cl2—Mo2—N3	83.6 (2)
Cl1—Mo1—N1	79.3 (2)	Cl2—Mo2—N4	79.4 (2)
Cl1—Mo1—N2	83.7 (2)	O2—Mo2—N3	86.8 (3)
O1—Mo1—N1	166.1 (2)	O2—Mo2—N4	164.9 (2)
O1—Mo1—N2	89.0 (3)	N3—Mo2—N4	78.7 (3)
N1—Mo1—N2	79.2 (3)	Mo1—S1—Mo2	75.80 (6)
S1—Mo2—S2	101.67 (7)	Mo1—S2—Mo2	75.37 (6)

Two of three pyridine solvent molecules have a site occupancy factor of 0.5. All atoms in the solvent molecules were refined isotropically. H atoms were not located.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *EQVRFL* (Imoto, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976) and *ANYBLK* (Imoto, 1989). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *ANYBLK*.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: CF1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 50–54

(Pyrazole-κN^2)[N-salicylidene-κO-(S)-alaninato-$\kappa^2 N,O$]copper(II) Dihydrate and (Pyrazole-κN^2)[N-salicylidene-κO-(R,S)-alaninato-$\kappa^2 N,O$]copper(II) Pyrazole Solvate

Salam A. Warda,[a]* Claus Friebel,[a] Julius Sivý,[b]
Gustav Plesch[c] and Maria Bláhová[d]

[a]*Department of Chemistry, Philipps University, D-35032 Marburg, Germany,* [b]*Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, 832 32 Bratislava, Slovakia,* [c]*Department of Inorganic Chemistry, Faculty of Natural Sciences, 842 15 Bratislava, Slovakia, and* [d]*Department of Chemical Theory of Drugs, Faculty of Pharmacy, Comenius University, 832 32 Bratislava, Slovakia*

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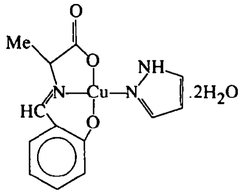
Abstract

In both {N-[(2-hydroxyphenyl)methylene]-(S)-alaninato-O,N,O'}(pyrazole-N^2)copper(II) dihydrate, $[Cu(C_{10}H_9NO_3)(C_3H_4N_2)].2H_2O$, (I), and {$N$-[(2-hydroxyphenyl)methylene]-(R,S)-alaninato-O,N,O'}(pyrazole-N^2)copper(II) pyrazole solvate, $[Cu(C_{10}H_9NO_3)(C_3H_4N_2)].C_3H_4N_2$, (II), the Cu^{II} ion adopts a similar axially distorted square-pyramidal coordination. The basal plane is formed by the tridentate Schiff base N-salicylidenealaninato dianion (TSB^{2-}) and the pyrazole ligand. The apex of the pyramid is occupied by a carboxylic O atom from the neighbouring chelate. The cooperative ordering and the apical distance [2.978 (3) Å in (I) compared with 2.366 (3) Å in (II)] are the two main differences between the two complexes. The stacked Cu(TSB) complexes within (I) form polymeric chains by translation parallel to [100]. The apically bridged Cu(TSB) complexes of (II) form zigzag chains parallel to [010] *via* the 2_1 operator. The influence of the configuration at the chiral C atoms as well as the effect of uncoordinated water and pyrazole molecules on the cooperative ordering are discussed.

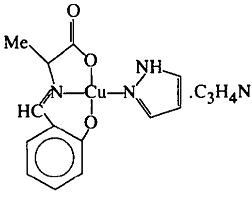
Comment

In complexes of general formula $[Cu(TSB)(L)].H_2O$, three donor atoms (O, N and O) of the TSB^{2-} dianion and a donor atom (O, N or S) of the neutral ligand L form a square-planar coordination around the Cu^{II} ion. Furthermore, an elongated square pyramid may be obtained by weak additional bonding of an O atom from the adjacent complex. Thus, either carboxylato-bridged chains (Ueki, Ashida, Sasada & Kakudo, 1967) or phenolic oxygen-bridged dimers (Warda, 1994) will result. Isolated complexes are obtained if an additional neutral molecule (*e.g.* water) coordinates at the apical position (Ueki, Ashida, Sasada & Kakudo, 1969).

The X-ray crystal structure investigations of the adducts of [N-salicylidene-(S)-alaninato]copper(II) with one pyrazole and two water molecules, (I), and of [N-salicylidene-(R,S)-alaninato]copper(II) with two pyrazole molecules, (II), were undertaken in order to detect whether water and pyrazole act as ligands or as solvent molecules. Kettmann, Frešova, Bláhová & Krätšmár-Šmogrovič (1993) reported recently the crystal structure of the optically active S enantiomer of complex (II). The influence of the chiral C atoms on the cooperative ordering of molecules was also of interest. Cooperative ordering, especially of Jahn–Teller ions, has been described using the term ferrodistortive for a parallel (2γ = 0°) and antiferrodistortive for a perpendicular (2γ = 90°) orientation; the angle 2γ describes the orientation of the main axes of polyhedra with respect to one another (Reinen & Friebel, 1979).



(I)



(II)

Complexes (I) and (II) both show axially extended square-planar coordination around the Cu^{II} ions. The atoms in the basal plane of the square-pyramid around the Cu^{II} atom belong to the Schiff base dianion (O1, N1 and O2) and the coordinated pyrazole molecule (N2) (Fig. 1). The apex is occupied by a carboxylic O atom from the adjacent molecule. There is a major difference, however, between the apical Cu—O distances in complexes (I) [2.798 (3) Å] and (II) [2.366(3) Å]. The different strength of axial interactions is reflected by the different displacements of the Cu atom from the basal plane towards the apices of the pyramids [0.084 (3) Å in (I) and 0.210 (3) Å in (II)].

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