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Mixed Chelate Complexes. II. Structures of L-Alaninato(aqua)(4,7-diphenyl-1,10-phenanthroline)copper(II) Nitrite Monohydrate and Aqua(4,7-dimethyl-1,10-phenanthroline)(glycinato)(nitrato)copper(II) Monohydrate

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Abstract. [Cu(C$_3$H$_6$NO$_2$)(C$_{24}$H$_{16}$N$_2$)(H$_2$O)]NO$_2$.H$_2$O (I), M_r = 566.1, monoclinic, $P2_1$, a = 11.864 (3), b = 7.726 (2), c = 14.832 (3) Å, β = 102.17 (2)°, V = 1329.0 (9) Å^3, Z = 2, D_x = 1.414 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 0.868 mm^{-1}, T = 288 K, R = 0.064 for 2061 reflections. [Cu(C$_2$H$_4$NO$_2$)(NO$_3$)(C$_{14}$H$_{12}$N$_2$)(H$_2$O)].H$_2$O (II), M_r = 443.9, triclinic, $P\bar{1}$, a = 14.138 (3), b = 10.016 (2), c = 7.565 (2) Å, α = 104.83 (2), β = 83.47 (2), γ = 119.93 (2)°, V = 897.3 (6) Å^3, Z = 2, D_x = 1.642 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ = 1.265 mm^{-1}, T = 288 K, R = 0.046 for 1322 reflections. The Cu ion displays square pyramidal coordination with an apical water molecule for (I) and a distorted octahedral coordination in (II). The apical Cu—OH$_2$ bond lengths are 2.209 (11) Å for (I) and 2.458 (6) Å for (II). The lengthening in (II) may be due to the trans O—NO$_2$ ligand that blocks the sixth coordination site. The results obtained are compared with those for other aminoacidate copper(II) complexes.

Introduction. Compounds with general formula [Cu(N–N)(O–N)H$_2$O]$^+$, where (N–N) = 4,7-di-

phenyl-1,10-phenanthroline or 4,7-dimethyl-1,10-phenanthroline and (O–N) = alaninato or glycinato, have been synthesized and characterized by Ruíz-Ramírez, Martínez & Gasque (1992) who also determined their stability constants potentiometrically. The compounds are obtained from 1:1 mmol solutions of Cu^{II} ion and the (N–N) ligand in water, followed by the addition of L-alanine (I) or glycine (II); the pH is increased to 8 by addition of ammonium hydroxide. Concentration of the solution leads to precipitation of the mixed chelate complex. Blue crystals are grown from a water solution. In order to determine the coordination geometry of the Cu^{II} ions and confirm the chelating scheme, crystal structure determinations have been carried out on the title compounds (I) and (II).

Experimental. A similar method was followed in the determination of both crystal structures. Prismatic crystal of (I) (0.1 × 0.1 × 0.15 mm) and tabular crystal of (II) (0.1 × 0.1 × 0.08 mm) were selected and mounted on a Philips PW1100 four-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Cell parameters were determined from 25 reflections (4 < θ < 12°) and refined by least squares. Intensities were collected with ω-scan technique, with scan width 1° and scan speed 0.03° s^{-1}.

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2235 independent reflections $(2 < \theta < 30°)$ for (I); (*hkl*) range: $-13-13$, $0-9$ and $0-13$; 2061 with $I > 2.5\sigma(I)$. 1476 independent reflections $(2 < \theta < 25°)$ for (II); (*hkl*) range: $-13-13$, $-11-11$ and $0-8$; 1322 with $I > 2.5\sigma(I)$, R_{int} (on F) = 0.045. Three intensities were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lp, but no absorption corrections were made.

In both structures Cu and several C, N and O atoms were located from *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and remaining non-H atoms with *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van den Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). Full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976). The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = \sigma^{-2}(F_o)$. f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–100 and 149). Final results for (I) correspond to the enantiomeric structure which gave the lower R value (0.064 *versus* 0.077). H-atom positions of (I) were not determined. 14 H-atom positions for (II) were computed and refined with an overall isotropic temperature factor, using a riding model. Number of refined parameters was 343 and 267, respectively. Max shift/e.s.d. of 0.05 for (I) and 0.1 for (II), max. and min. peaks in final difference synthesis are 0.4 and -0.03 e Å^{-3} in both structures.

Discussion. Final atomic coordinates and equivalent isotropic thermal coefficients are given in Table 1.* Table 2 shows bond lengths and angles. Figs. 1 and 2 present views of structures (I) and (II), respectively, with atom numbering.

In (I) the Cu ion displays a square pyramidal coordination, being linked to the O(1) and N(5) atoms of the alaninato ligand and two N atoms of the 4,7-diphenyl-1,10-phenanthroline ligand in the basal plane, and an O atom of a water molecule in the apical site. In (II) the Cu ion displays a similar coordination, but O(3) of the nitrato group is weakly linked to the Cu ion *trans* to the apical water molecule. This feature has been observed previously (Solans, Ruíz-Ramírez, Gasque & Briansó, 1987; Solans, Aguiló, Gleizest, Faus, Julve & Verdaguer, 1990) but the Cu—O(3) bond length of 2.645 (5) Å in (II) is short compared with previously determined values of 2.781 (3) and 2.998 (3) Å. The basal N_3O donor set defines a more or less puckered plane

Table 1. *Final atomic coordinates* [$\times 10^4$, Cu $\times 10^5$ *for* (I)] *and equivalent isotropic thermal coefficients* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I)				
Cu	62505 (11)	51640	75783 (9)	3.39 (6)
O(1)	5407 (7)	6139 (15)	6402 (5)	4.18 (44)
O(2)	4049 (8)	7890 (14)	5756 (7)	5.01 (49)
C(3)	4560 (10)	7142 (19)	6404 (8)	3.08 (55)
C(4)	4259 (12)	7502 (19)	7338 (9)	3.98 (64)
N(5)	5130 (10)	6633 (20)	8125 (7)	5.01 (65)
C(6)	3018 (9)	7039 (29)	7199 (10)	5.95 (86)
N(11)	7593 (8)	4463 (13)	7016 (7)	3.12 (47)
C(12)	7640 (10)	4324 (16)	6170 (7)	2.69 (53)
C(13)	8619 (10)	3929 (17)	5827 (10)	4.05 (61)
C(14)	9611 (10)	3710 (16)	6521 (7)	2.77 (54)
C(15)	9618 (8)	3848 (15)	7401 (9)	2.87 (52)
C(16)	10642 (10)	3578 (17)	8224 (10)	3.81 (60)
C(17)	10572 (9)	3729 (18)	9050 (9)	3.47 (58)
C(18)	9462 (9)	4155 (16)	9349 (8)	2.96 (53)
C(19)	9273 (11)	4345 (19)	10268 (8)	3.76 (60)
C(20)	8207 (10)	4620 (18)	10401 (8)	3.43 (59)
C(21)	7193 (11)	4884 (20)	9614 (11)	5.02 (75)
N(22)	7357 (9)	4748 (15)	8730 (6)	3.76 (56)
C(23)	8440 (10)	4431 (16)	8577 (9)	3.05 (55)
C(24)	8537 (9)	4229 (17)	7663 (7)	2.70 (51)
C(41)	10716 (11)	3458 (19)	6120 (8)	3.58 (60)
C(42)	10938 (13)	4645 (17)	5486 (9)	4.21 (70)
C(43)	11916 (13)	4349 (20)	5157 (8)	4.11 (65)
C(44)	12756 (11)	3038 (20)	5488 (10)	3.99 (66)
C(45)	12482 (11)	1832 (20)	6149 (13)	5.78 (82)
C(46)	11484 (11)	2040 (20)	6449 (7)	3.53 (60)
C(91)	10193 (11)	4157 (15)	11108 (8)	3.05 (54)
C(92)	9947 (13)	3339 (17)	11870 (9)	4.28 (65)
C(93)	10904 (17)	3355 (25)	12795 (14)	6.71 (104)
C(94)	11960 (17)	4155 (25)	12713 (14)	7.59 (103)
C(95)	12224 (12)	4950 (27)	11930 (10)	5.32 (74)
C(96)	11281 (10)	4990 (19)	11099 (9)	4.05 (58)
O(W1)	5341 (8)	2653 (15)	7467 (10)	6.93 (66)
O(W2)	5513 (10)	958 (16)	5779 (7)	5.82 (56)
O(31)	3581 (10)	3681 (27)	191 (10)	8.34 (89)
N(32)	3813 (15)	4631 (21)	-213 (15)	8.67 (107)
O(33)	4594 (10)	5337 (34)	-149 (13)	12.09 (117)
(II)				
Cu	7251 (1)	247 (1)	6110 (2)	2.87 (6)
O(1)	7050 (10)	-1662 (10)	4274 (12)	6.61 (58)
C(2)	6101 (9)	-2672 (10)	3933 (12)	2.23 (45)
O(2)	5805 (8)	-3893 (9)	2646 (10)	5.17 (46)
C(3)	5239 (11)	-2594 (12)	5190 (16)	4.50 (61)
N(4)	5628 (9)	-1075 (10)	6713 (11)	3.81 (48)
N(5)	8826 (7)	1469 (8)	5490 (10)	2.06 (37)
C(6)	9465 (12)	1032 (12)	4366 (15)	4.02 (62)
C(7)	10557 (9)	1993 (10)	4156 (12)	2.35 (44)
C(8)	11051 (9)	3525 (10)	5173 (12)	2.23 (47)
C(9)	10398 (9)	4091 (9)	6329 (11)	2.13 (43)
C(10)	10768 (11)	5674 (12)	7296 (14)	3.37 (56)
C(11)	10120 (12)	6155 (13)	8325 (15)	3.79 (62)
C(12)	8968 (8)	5076 (9)	8610 (11)	1.78 (38)
C(13)	8169 (9)	5522 (10)	9718 (12)	2.78 (48)
C(14)	7174 (9)	4367 (10)	9750 (11)	2.36 (44)
C(15)	6986 (10)	2797 (11)	8751 (12)	3.14 (52)
N(16)	7610 (9)	2415 (9)	7639 (11)	2.94 (44)
C(17)	8634 (8)	3546 (9)	7626 (11)	1.51 (40)
C(18)	9257 (9)	3051 (10)	6410 (12)	2.28 (45)
C(81)	12165 (11)	4536 (13)	5007 (15)	4.03 (63)
C(131)	8551 (12)	7193 (13)	10600 (16)	4.60 (69)
O(W1)	7885 (7)	-603 (8)	8283 (10)	4.04 (39)
O(21)	7513 (10)	746 (10)	1694 (12)	5.78 (55)
N(22)	6588 (12)	424 (12)	2208 (15)	4.29 (61)
O(3)	6317 (10)	840 (11)	3797 (12)	6.41 (66)
O(24)	5769 (9)	-336 (11)	1081 (13)	6.67 (57)

[average deviations from the mean N_3O plane are ± 0.03 (2) Å for (I) and 0.067 (6) Å for (II)] while the Cu ion is 0.293 (6) and 0.064 (4) Å out of this plane for (I) and (II), respectively. It can be observed that the smaller deviation occurs in the compound where copper is six coordinate.

Table 2. Bond lengths (Å) and angles (°)

(I)

O(1)—Cu	1.969 (8)	C(23)—C(18)	1.497 (16)
N(5)—Cu	2.041 (11)	C(20)—C(19)	1.337 (17)
N(11)—Cu	2.022 (10)	C(91)—C(19)	1.481 (17)
N(22)—Cu	1.949 (10)	C(21)—C(20)	1.503 (17)
O(W1)—Cu	2.209 (11)	N(22)—C(21)	1.369 (18)
C(3)—O(1)	1.270 (15)	C(23)—N(22)	1.372 (14)
C(3)—O(2)	1.175 (14)	C(24)—C(23)	1.394 (17)
C(4)—C(3)	1.528 (18)	C(42)—C(41)	1.377 (18)
N(5)—C(4)	1.540 (17)	C(46)—C(41)	1.443 (18)
C(6)—C(4)	1.487 (16)	C(43)—C(42)	1.370 (18)
C(12)—N(11)	1.272 (14)	C(44)—C(43)	1.433 (19)
C(24)—N(11)	1.325 (14)	C(45)—C(44)	1.439 (22)
C(13)—C(12)	1.397 (17)	C(46)—C(45)	1.359 (19)
C(14)—C(13)	1.400 (16)	C(92)—C(91)	1.379 (17)
C(15)—C(14)	1.308 (16)	C(96)—C(91)	1.446 (18)
C(41)—C(14)	1.562 (16)	C(93)—C(92)	1.585 (23)
C(16)—C(15)	1.544 (14)	C(94)—C(93)	1.425 (27)
C(24)—C(15)	1.446 (16)	C(95)—C(94)	1.406 (25)
C(17)—C(16)	1.251 (18)	C(96)—C(95)	1.480 (15)
C(18)—C(17)	1.511 (16)	N(32)—O(31)	1.021 (19)
C(19)—C(18)	1.436 (18)	O(33)—N(32)	1.063 (20)

N(5)—Cu—O(1)	83.5 (4)	C(23)—C(18)—C(19)	116.6 (10)
N(11)—Cu—O(1)	92.0 (4)	C(20)—C(19)—C(18)	119.9 (11)
N(11)—Cu—N(5)	161.6 (5)	C(91)—C(19)—C(18)	123.7 (11)
N(22)—Cu—O(1)	164.2 (4)	C(91)—C(19)—C(20)	116.4 (11)
N(22)—Cu—N(5)	96.8 (4)	C(21)—C(20)—C(19)	122.3 (11)
N(22)—Cu—N(11)	82.7 (4)	N(22)—C(21)—C(20)	118.8 (12)
O(W1)—Cu—O(1)	86.9 (5)	C(21)—N(22)—Cu	128.4 (8)
O(W1)—Cu—N(5)	99.7 (5)	C(23)—N(22)—Cu	111.5 (8)
O(W1)—Cu—N(11)	98.5 (4)	C(23)—N(22)—C(21)	119.9 (11)
O(W1)—Cu—N(22)	98.6 (5)	N(22)—C(23)—C(18)	122.3 (10)
C(3)—O(1)—Cu	119.1 (7)	C(24)—C(23)—C(18)	120.5 (10)
O(2)—C(3)—O(1)	124.8 (12)	C(24)—C(23)—N(22)	116.9 (11)
C(4)—C(3)—O(1)	116.8 (10)	C(15)—C(24)—N(11)	119.7 (10)
C(4)—C(3)—O(2)	118.3 (12)	C(23)—C(24)—N(11)	117.3 (11)
N(5)—C(4)—C(3)	111.1 (11)	C(23)—C(24)—C(15)	122.9 (10)
C(6)—C(4)—C(3)	104.1 (11)	C(42)—C(41)—C(14)	118.3 (12)
C(6)—C(4)—N(5)	119.2 (12)	C(46)—C(41)—C(14)	119.1 (11)
C(4)—N(5)—Cu	109.3 (8)	C(46)—C(41)—C(42)	122.6 (12)
C(12)—N(11)—Cu	129.2 (8)	C(43)—C(42)—C(41)	115.5 (13)
C(24)—N(11)—Cu	110.9 (8)	C(44)—C(43)—C(42)	125.2 (12)
C(24)—N(11)—C(12)	119.8 (11)	C(45)—C(44)—C(43)	116.8 (11)
C(13)—C(12)—N(11)	126.2 (11)	C(46)—C(45)—C(44)	119.0 (12)
C(14)—C(13)—C(12)	113.1 (12)	C(45)—C(46)—C(41)	120.7 (13)
C(15)—C(14)—C(13)	123.5 (12)	C(92)—C(91)—C(19)	119.2 (12)
C(41)—C(14)—C(13)	112.2 (10)	C(96)—C(91)—C(19)	116.7 (11)
C(41)—C(14)—C(15)	124.1 (10)	C(96)—C(91)—C(92)	123.8 (12)
C(16)—C(15)—C(14)	128.0 (11)	C(93)—C(92)—C(91)	117.9 (13)
C(24)—C(15)—C(14)	117.7 (9)	C(94)—C(93)—C(92)	114.3 (16)
C(24)—C(15)—C(16)	114.2 (11)	C(95)—C(94)—C(93)	127.8 (14)
C(17)—C(16)—C(15)	123.9 (12)	C(96)—C(95)—C(94)	115.9 (13)
C(18)—C(17)—C(16)	123.3 (10)	C(95)—C(96)—C(91)	120.1 (13)
C(19)—C(18)—C(17)	128.4 (10)	O(33)—N(32)—O(31)	130.8 (26)
C(23)—C(18)—C(17)	115.0 (10)		

Table 2 (cont.)

O(W1)—Cu—C(2)	95.7 (2)	C(14)—C(13)—C(12)	116.0 (7)
O(W1)—Cu—N(4)	93.3 (3)	C(131)—C(13)—C(12)	118.4 (8)
O(W1)—Cu—N(5)	86.1 (3)	C(131)—C(13)—C(14)	125.6 (10)
O(W1)—Cu—N(16)	98.1 (3)	C(15)—C(14)—C(13)	115.6 (9)
C(2)—O(1)—Cu	114.4 (9)	N(16)—C(15)—C(14)	129.2 (9)
O(1)—C(2)—Cu	41.4 (6)	C(15)—N(16)—Cu	127.5 (7)
O(2)—C(2)—Cu	163.7 (7)	C(17)—N(16)—Cu	116.5 (7)
O(2)—C(2)—O(1)	123.6 (10)	C(17)—N(16)—C(15)	115.7 (7)
C(3)—C(2)—Cu	79.5 (5)	N(16)—C(17)—C(12)	121.4 (9)
C(3)—C(2)—O(1)	119.6 (8)	C(18)—C(17)—C(12)	125.7 (8)
C(3)—C(2)—O(2)	116.4 (8)	C(18)—C(17)—N(16)	112.5 (7)
N(4)—C(3)—C(2)	114.8 (8)	C(9)—C(18)—N(5)	119.0 (9)
C(3)—N(4)—Cu	102.9 (6)	C(17)—C(18)—N(5)	120.5 (8)
C(6)—N(5)—Cu	131.5 (6)	C(17)—C(18)—C(9)	119.6 (7)
C(18)—N(5)—Cu	109.9 (6)	O(23)—N(22)—O(21)	126.4 (10)
C(18)—N(5)—C(6)	118.6 (8)	O(24)—N(22)—O(21)	121.6 (10)
C(7)—C(6)—N(5)	124.8 (8)	O(24)—N(22)—O(23)	111.9 (14)
C(8)—C(7)—C(6)	119.0 (9)		

(II)

O(1)—Cu	1.963 (8)	C(10)—C(9)	1.410 (11)
C(2)—Cu	2.703 (7)	C(18)—C(9)	1.424 (12)
N(4)—Cu	2.065 (9)	C(11)—C(10)	1.328 (16)
N(5)—Cu	2.004 (8)	C(12)—C(11)	1.467 (14)
N(16)—Cu	2.014 (7)	C(13)—C(12)	1.509 (13)
O(W1)—Cu	2.458 (6)	C(17)—C(12)	1.378 (9)
C(2)—O(1)	1.217 (12)	C(14)—C(13)	1.303 (12)
O(2)—C(2)	1.261 (9)	C(131)—C(13)	1.466 (11)
C(3)—C(2)	1.480 (15)	C(15)—C(14)	1.461 (11)
N(4)—C(3)	1.535 (10)	N(16)—C(15)	1.279 (13)
C(6)—N(5)	1.326 (14)	C(17)—N(16)	1.321 (11)
C(18)—N(5)	1.391 (9)	C(18)—C(17)	1.373 (12)
C(7)—C(6)	1.370 (14)	N(22)—O(21)	1.222 (14)
C(8)—C(7)	1.372 (10)	O(23)—N(22)	1.250 (13)
C(9)—C(8)	1.422 (13)	O(24)—N(22)	1.288 (11)
C(81)—C(8)	1.396 (14)		

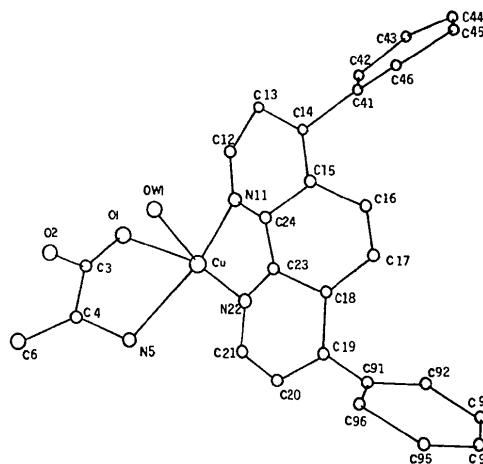|			
C(2)—Cu—O(1)	24.2 (4)	C(9)—C(8)—C(7)	118.8 (8)
N(4)—Cu—O(1)	86.1 (4)	C(81)—C(8)—C(7)	120.6 (9)
N(4)—Cu—C(2)	62.7 (3)	C(81)—C(8)—C(9)	120.5 (8)
N(5)—Cu—O(1)	92.2 (4)	C(10)—C(9)—C(8)	125.0 (8)
N(5)—Cu—C(2)	115.7 (3)	C(18)—C(9)—C(8)	119.2 (7)
N(5)—Cu—N(4)	178.3 (3)	C(18)—C(9)—C(10)	115.5 (9)
N(16)—Cu—O(1)	169.6 (3)	C(11)—C(10)—C(9)	122.9 (10)
N(16)—Cu—C(2)	159.7 (4)	C(12)—C(11)—C(10)	122.9 (9)
N(16)—Cu—N(4)	101.5 (4)	C(13)—C(12)—C(11)	126.5 (7)
N(16)—Cu—N(5)	80.2 (3)	C(17)—C(12)—C(11)	112.4 (8)
O(W1)—Cu—O(1)	88.4 (3)	C(17)—C(12)—C(13)	120.9 (7)

Fig. 1. A molecular view of (alaninato)aqua(4,7-diphenyl-1,10-phenanthroline)copper(II) nitrite monohydrate.
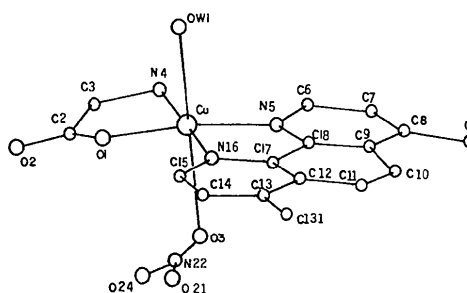
Fig. 2. A molecular view of aqua(4,7-dimethyl-1,10-phenanthroline)(glycinato)(nitrato)copper(II) monohydrate.

The average Cu—N(ar) bond length of 2.00 (2) Å is similar to those observed in many related compounds (Aoki & Yamasaky, 1980; Solans, Ruíz-Ramírez, Gasque & Briansó, 1987; Solans, Ruíz-Ramírez, Martínez, Gasque & Briansó, 1988; Solans, Aguiló, Gleizest, Faus, Julve & Verdaguer, 1990;

Antolini, Macrotrigiano, Menabue & Pellacani, 1983; Solans, Ruíz-Ramírez, Martínez, Gasque & Moreno-Esparza, 1992) though longer Cu—N(ar) distances of up to 2.145 (2) Å have been reported (Nardin, Randaccio, Bonomo & Rizzarelli, 1980).

The Cu—O(1) (carboxylate) and Cu—N (aminoacidato) bond lengths in (I) and (II) are slightly longer than those observed in related complexes (Solans, Ruíz-Ramírez, . Martínez, Gasque & Briansó, 1988; Antolini, Marcotrigiano, Menabue & Pellacani, 1983).

The Cu—O(W1) (aqua) apical bond length alters from 2.209 (11) in (I) to 2.458 (6) Å in (II). Values of 2.24 (1) and 2.368 (5) Å are reported for aqua(1,10-phenanthroline)(L-phenylalaninato)copper(II) nitrate monohydrate (Solans, Ruíz-Ramírez, Martínez, Gasque & Briansó, 1988) and aqua(aspartato)-(2,2'-bipyridine)copper(II) trihydrate (Antolini, Marcotrigiano, Menabue & Pellacani, 1983), respectively.

The N(5)—Cu—O(1) bond angle of 83.5 (4)° in (I) and the N(4)—Cu—O(1) angle of 86.1 (4)° in (II) correlate with the mean metal–ligand bond lengths in (I) and (II) (2.055 and 2.014 Å, respectively). This correlation is based on the constancy of the O(1)···N(5) and O(1)···N(4) distances (average 2.66 Å). The mean donor–metal distance increases linearly from 2.0 to 2.5 Å as the interionic angle decreases from 84 to 64° (Freeman, 1967).

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Structural Characterization of W—^{4}—WCl₄(PMePh₂)₄

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Abstract. Bis[dichlorobis(methyldiphenylphosphine-P)tungsten](W—^{4}—W) benzene solvate, [W₂Cl₄(C₁₃H₁₃P)₄], M_r = 1388.64, orthorhombic, $Pbca$, a = 12.2783 (8), b = 21.5387 (6), c = 41.9626 (2) Å, V = 11097 (8) Å³, Z = 8, D_x = 1.664 g cm⁻³, λ(Mo $K\alpha$) = 0.71073 Å, μ = 45.827 cm⁻¹, $F(000)$ = 5456, T = 173 K, R = 0.0435 for 4359 unique observed reflections. The molecule is dinuclear with a W—^{4}—W distance of 2.2728 (7) Å. The W—Cl distances range from 2.373 (4) to 2.398 (4) Å and the W—P distances from 2.529 (4) to 2.548 (4) Å. The angles between the trans Cl ligands are 139.9 (1) and 137.3 (1)° for Cl(1)—W(1)—Cl(2) and Cl(3)—W(2)—Cl(4), respectively. The angles between the trans phosphine ligands are 158.2 (1) and 156.0 (1)° for P(1)—W(1)—P(2) and P(3)—W(2)—P(4), respectively.

Introduction. While quadruply bonded dimolybdenum compounds have been extensively studied, the

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