significantly weaker and s therefore smaller, with a value of 0·32 (McCarron, Whitney & Chase, 1984). In the former cases such behaviour reflects the presence, in the latter the absence of an electrostatic component to the bonding.

The O—Mo—O bond angles vary from 69·0 (1) to 105·4 (2)°, indicating the distortion of the MoO_6 octahedra. The N—C—S anion is not linear; the angle at C amounts to 177·8 (5)°.

Potassium ion K(1) is irregularly surrounded by eight O atoms, six from octamolybdate anions and two from water molecules, at distances varying from 2·711 (5) to 3·132 (4) Å. Potassium ion K(2) is at the same time surrounded by four octamolybdate O atoms [from 2·736 (5) to 2·954 (4) Å], one water O atom [2·821 (6) Å] and two isothiocyanato S atoms at 3·320 (2) and 3·376 (2) Å, while K(3) is similarly surrounded by four octamolybdate O atoms [from 2·730 (4) to 3·102 (4) Å], two water O [2·720 (7) and 2·874 (7) Å] and one S at 3·311 (2) Å. The polyhedra around the K ions form a column extended along the crystallographic a axis.

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A New Tetraamidodimolybdenum Complex with a Quadruple $M—M$ Bond

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Abstract. Tetrakis-μ-(N-*tert*-butylacetamido-O,N)-dimolybdenum(II)(*Mo—Mo*), [$Mo_2(C_6H_{12}NO)_4$], $M_r = 648\cdot56$, orthorhombic, *Pbca*, $a = 12\cdot475$ (2), $b = 15\cdot073$ (4), $c = 15\cdot876$ (2) Å, $V = 2985\cdot2$ Å^3, $Z = 4$, $D_x = 1\cdot44$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 8\cdot5$ cm^{-1}, $F(000) = 1344$, $T = 296$ (2) K, $R = 0\cdot045$ for 1546 observed reflections. The molecule is a quadruple-bonded dimer of crystallographic $\bar{1}$ (C_i) site symmetry. Each N-*tert*-butylacetamide ligand bridges the dimolybdenum core with its N atom bound to one metal and its O atom bound to the other metal. The four bridging ligands are arranged such that the two N atoms and the two O atoms bound to each Mo atom are in a *cis* conformation. The Mo—Mo distance of 2·063 (1) Å is among the shortest reported Mo—Mo quadruple-bond distances.

Introduction. A plethora of $M—M$ multiple-bonded complexes with a diverse range of bridging-ligand types has been characterized to examine the factors which contribute to the bonding in $M—M$ multiple-bonded complexes (Cotton & Walton, 1982, 1985). Multiple-bonded dimers with N and O donor atoms in the ligand set have been prepared for each member of the chromium, molybdenum, and tungsten triad, and photoelectron spectroscopy study of these complexes has provided important insights into metal–metal multiple bonding (Bursten, Cotton, Cowley, Hanson, Lattman & Stanley, 1979). However, many of the known compounds in this class contain large organic-ring π groups (*i.e.* benzene and pyridine rings) with ionizations which obscure important metal-based ionization features in the photoelectron spectrum. From our

experience in examining the electronic structure relationships of multiple-bonded complexes by photoelectron spectroscopy (Lichtenberger & Kristofzski, 1987), we believe that important questions can be answered if similar multiple-bonded complexes, without relatively large rigid organic rings in the ligand set, can be synthesized and characterized. The title complex represents the first result of these synthetic efforts.

Experimental. 0.28 g of N-tert-butylacetamide (tbace) was dissolved in 30 ml of tetrahydrofuran freshly distilled from K, and the solution was cooled in an ice bath. 1.6 ml of 1.55 M n-butyllithium in hexane was slowly added. The solution was warmed to room temperature and 0.25 g of [Mo$_2$(O$_2$CCH$_3$)$_4$] was slowly added. The solution was then stirred under N$_2$ for 24 h at room temperature. The lithium acetate precipitate was removed by filtering, and the resulting solution was evaporated to dryness and sublimed in vacuo. The yellow, waxy compound on the cold finger was dissolved in CH$_2$Cl$_2$, and crystals were grown in a 243 K freezer over 2 d. A mass spectrum showed a strong parent-ion isotope pattern.

A yellow, rectangular crystal of approximate dimensions 0.17 × 0.25 × 0.35 mm was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed on a Syntex P2$_1$ diffractometer equipped with a highly oriented graphite incident-beam monochromator. Cell constants and orientation matrix for data collection were obtained from 20 reflections in the range 11 < 2θ < 22°. The systematic absences: hk0 h = 2n + 1; h0l l = 2n + 1 and 0kl k = 2n + 1 determine the space group Pbca (No. 61). Data were collected to a maximum 2θ of 55.0° (h = 0–17, k = 0–20, l = 0–21) with 2θ–θ scans. The 2θ scan rate varied from 2 to 8° min⁻¹. The scan range was (2θ$_2$ − 1°) − (2θ$_1$ + 1°).

The ratio of scan time to background time was 2:1. 4081 reflections were collected, of which 3445 were unique and not systematically absent. The intensities of three check reflections, measured after every 46 reflections, remained constant (≤ −0.3%). Lorentz and polarization corrections, but no absorption correction (ψ scans ≤ 6.2% variation from mean) were applied to the data. The agreement factor for the averaging of 86 multiply observed reflections was 5.2% based on intensity and 3.1% based on F$_o$.

The structure was solved via the Patterson heavy-atom method which revealed the position of the Mo atom. The remaining atoms were located in succeeding difference Fourier maps. H atoms were included, with idealized geometries (C—H = 0.95 Å), in the refinement but constrained (with fixed isotropic thermal parameters) to ride on the atom to which they are bonded.

The structure was refined with full-matrix least squares where the function minimized was $\sum w(|F_o| -$

$|F_c|)^2$. The weights were $w = 4F^2/[\sigma^2(I) + (pF^2)^2]$, with $p = 0.04$, and $\sigma(I)$ from counting statistics. Atomic scattering factors were taken from Cromer & Waber (1974). Anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964); the values for f' and f'' were those of Cromer (1974). Only the 1546 reflections with $I > 3\sigma(I)$ were used in the refinements. In the final cycle 154 parameters were varied, maximum shift/e.s.d. was 0.1; unweighted and weighted factors $R = 0.039$, $wR = 0.041$. The standard deviation of an observation of unit weight was 1.13. The three correlation coefficients greater than 0.50 were between the overall scale factor and the thermal parameters of Mo. The maximum excursions in final difference Fourier synthesis had heights of 0.50 and −0.57 e Å⁻³ with $\sigma(\Delta F)$ of 0.11 (Cruickshank, 1949). Plots of $\sum w(|F_o| - |F_c|)$ versus $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$ and various classes of indices showed no unusual trends. All calculations were performed on a VAX computer with SDP/VAX (Frenz, 1978).

Discussion. The compound crystallizes with the center of the M—M bond on an inversion center. The atomic coordinates and bond distances and angles of the independent half-molecule are given in Tables 1 and 2, respectively.* Fig. 1 shows the atomic numbering.

Each N-tert-butylacetamide ligand bridges the dimolybdenum core with its N atom bound to one metal and its O atom bound to the other metal. The four bridging ligands are arranged such that the two N atoms and the two O atoms bound to each metal are in a cis conformation. This is uncommon for bridged complexes with different donor atoms (N, O; N, S; N, N') in the ligand. The cis conformation is commonly seen when C and O are the donor atoms in the bridging ligand (Bino, Cotton & Kaim, 1979). The Mo—Mo distance of 2.063 (1) Å is shorter than those reported for other amidato-bridged Mo compounds (Cotton & Walton, 1982). Two compounds, [Mo$_2$(mhp)$_4$].CH$_2$Cl$_2$ and [Mo$_2$(dmp)$_4$], have comparable Mo—Mo bond lengths of 2.065 (1) and 2.064 (1) Å, respectively (Cotton & Walton, 1982) (mhp = 6-methyl-2-hydroxypyridine anion; dmp = 2,6-dimethoxyphenyl anion). Only the complex [Mo$_2${(C$_5$NH$_4$)NC(O)CH$_3$}$_4$] has a clearly shorter Mo—Mo bond length at 2.037 (3) Å (Cotton, Ilsley & Kaim, 1979). The mean Mo—N and Mo—O distances of 2.205 (6) and 2.085 (4) Å and the mean M—M—L (L = O, N) bond angles of 94.5 (2) and

Table 1. *Positional parameters, equivalent isotropic thermal parameters and their e.s.d.'s*

$$B_{eq} = \tfrac{1}{3}\sum_i\sum_j B_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Mo	0.47270 (4)	0.44101 (3)	0.47499 (3)	2.189 (7)
O(1)	0.6880 (3)	0.5200 (3)	0.5254 (3)	2.91 (9)
O(2)	0.5580 (3)	0.6174 (3)	0.4086 (3)	2.9 (1)
N(1)	0.6351 (4)	0.3837 (3)	0.4830 (3)	2.6 (1)
N(2)	0.4870 (4)	0.4966 (3)	0.3464 (3)	2.5 (1)
C(1)	0.7106 (5)	0.4397 (5)	0.5067 (4)	2.7 (1)
C(2)	0.5302 (6)	0.5759 (4)	0.3420 (4)	3.2 (1)
C(3)	0.6556 (5)	0.2856 (4)	0.4731 (5)	3.5 (1)
C(4)	0.4379 (5)	0.4519 (4)	0.2712 (4)	3.2 (1)
C(11)	0.8306 (5)	0.4224 (5)	0.5134 (5)	4.6 (2)
C(21)	0.5561 (7)	0.6277 (5)	0.2622 (5)	5.4 (2)
C(31)	0.7222 (7)	0.2668 (5)	0.3934 (5)	6.0 (2)
C(32)	0.5489 (6)	0.2399 (4)	0.4629 (6)	4.9 (2)
C(33)	0.7082 (8)	0.2466 (5)	0.5512 (6)	6.4 (2)
C(41)	0.3748 (7)	0.3711 (5)	0.3032 (5)	5.6 (2)
C(42)	0.5236 (8)	0.4177 (6)	0.2096 (5)	6.5 (2)
C(43)	0.3541 (7)	0.5089 (5)	0.2281 (6)	6.2 (2)

Fig. 1. *ORTEP* view (Johnson, 1976) showing 50% probability ellipsoids.

Table 2. *Bond distances (Å) and bond angles (°), e.s.d.'s in parentheses*

Mo	Mo	2.063 (1)	N(2)	C(4)	1.502 (8)
Mo	O(1)	2.090 (4)	C(1)	C(11)	1.523 (8)
Mo	O(2)	2.082 (4)	C(2)	C(21)	1.523 (9)
Mo	N(1)	2.206 (5)	C(3)	C(31)	1.54 (1)
Mo	N(2)	2.214 (6)	C(3)	C(32)	1.507 (9)
O(1)	C(1)	1.278 (8)	C(3)	C(33)	1.52 (1)
O(2)	C(2)	1.278 (8)	C(4)	C(41)	1.54 (1)
N(1)	C(1)	1.319 (8)	C(4)	C(42)	1.54 (1)
N(1)	C(3)	1.509 (8)	C(4)	C(43)	1.52 (1)
N(2)	C(2)	1.312 (8)			

Mo	Mo	O(1)	94.3 (1)	O(1)	C(1)	N(1)	121.0 (6)
Mo	Mo	O(2)	94.8 (1)	O(1)	C(1)	C(11)	111.2 (6)
Mo	Mo	N(1)	90.7 (1)	N(1)	C(1)	C(11)	127.8 (7)
Mo	Mo	N(2)	90.1 (1)	O(2)	C(2)	N(2)	120.8 (6)
O(1)	Mo	O(2)	86.9 (2)	O(2)	C(2)	C(21)	112.3 (6)
O(1)	Mo	N(1)	172.6 (2)	N(2)	C(2)	C(21)	126.8 (7)
O(1)	Mo	N(2)	88.2 (2)	N(1)	C(3)	C(31)	110.9 (7)
O(2)	Mo	N(1)	87.3 (2)	N(1)	C(3)	C(32)	108.0 (5)
O(2)	Mo	N(2)	173.3 (2)	N(1)	C(3)	C(33)	111.5 (7)
N(1)	Mo	N(2)	97.3 (2)	C(31)	C(3)	C(32)	107.7 (7)
Mo	O(1)	C(1)	118.5 (4)	C(31)	C(3)	C(33)	111.5 (7)
Mo	O(2)	C(2)	118.5 (4)	C(32)	C(3)	C(33)	107.0 (7)
Mo	N(1)	C(1)	115.0 (4)	N(2)	C(4)	C(41)	107.6 (5)
Mo	N(1)	C(3)	122.2 (4)	N(2)	C(4)	C(42)	111.9 (6)
C(1)	N(1)	C(3)	122.4 (6)	N(2)	C(4)	C(43)	112.7 (6)
Mo	N(2)	C(2)	115.3 (5)	C(41)	C(4)	C(42)	107.5 (7)
Mo	N(2)	C(4)	122.0 (4)	C(41)	C(4)	C(43)	104.1 (7)
C(2)	N(2)	C(4)	122.2 (6)	C(42)	C(4)	C(43)	112.4 (7)

Fig. 2. *ORTEP* view (Johnson, 1976) parallel to Mo—Mo bond axis.

90.4 (2)°, respectively, are comparable (3σ) to those reported for analogous amidato-bridged compounds. The N(1)—Mo—N(2) angle is 97.3 (2)°, while the O(1)—Mo—O(2) angle is 86.9 (2)°. This distortion from 90° angles is clearly seen from the end-on view of the molecule in Fig. 2. The larger N—*M*—N angle is presumably due to steric repulsion between the bulky *tert*-butyl groups that are bound to the *cis* N atoms. This angle is over twice as large as that observed for analogous *N*-phenyl ligands, graphically illustrating the bulky nature of the *tert*-butyl substituent *versus* the phenyl moiety.

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Structure of (2-Acetylpyrrolato){N-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II)

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Abstract. $[Cu(C_8H_{11}N_2)(C_6H_6NO)]$, $M_r = 306.86$, orthorhombic, $Pbca$, $a = 7.146$ (1), $b = 19.762$ (3), $c = 19.443$ (4) Å, $V = 2753$ (1) Å³, $Z = 8$, $D_x = 1.481$ Mg m⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 1.58$ mm⁻¹, $F(000) = 1272$, $T = 293$ (1) K, $R = 0.032$ for 1015 observed reflections with $I > 3\sigma(I)$. The Cu atom is coordinated to two different bidentate ligands and has distorted square-planar geometry with a Cu—O distance of 2.022 (2) and Cu—N distances of 1.942 (3) (*trans* to O), 1.980 (3) and 1.935 (3) Å, and angles O—Cu—N(2) 91.5 (1), O—Cu—N(3) 82.2 (1), N(1)—Cu—N(2) 82.6 (1) and N(1)—Cu—N(3) 103.8 (1)°.

Introduction. Crystal structures of several bis(2-pyrrolylmethylenamine)–metal complexes, prepared by the interaction of tertiary butylamine Schiff-base derivatives of 2-pyrrolecarbaldehyde with Zn[II] (Kanters, Spek, Postma, van Stein & van Koten, 1983), Cu[II] (Wei, 1972a), Ni[II] (Wei & Einstein, 1972) and Co[II] (Wei, 1972b) ions, have been reported in recent years. Syntheses and solution studies have been performed on metal complexes of other Schiff-base derivatives of 2-pyrrolecarbaldehyde (Holm, Chakravorty & Theriot, 1966; Yeh & Barker, 1967), as well as on the products of the direct substitution of 2-pyrrolecarbaldehyde and 2-acetylpyrrole on Cr[III], Cu[II] and Co[III] metal centers (Davies & Gogan, 1972; Habeeb, Tuck & Walters, 1978; Perry & Weber, 1971).

In the present study, bis{N-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II) was synthesized by published methods (Holm *et al.*, 1966; Yeh & Barker, 1967) and allowed to hydrolyze slowly in air to produce a mixed-ligand product containing one ethylamine Schiff base and one 2-acetylpyrrole chelate per metal center. The title compound is the result of a novel synthetic pathway to the formation of 2-acetylpyrrole chelate complexes of Cu[II], as well as an interesting example of a mixed-ligand copper adduct.

Experimental. Bis{N-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II) was synthesized by the 1:1 interaction of 2-acetylpyrrole with $CuSO_4.5H_2O$ in 35% ethylamine/H_2O. The blue product slowly turned light brown in air (3–5 d), and was subsequently recrystallized from petroleum ether to yield black crystals of $[Cu(C_8H_{11}N_2)(C_6H_6NO)]$. Analysis: calculated for $C_{14}H_{17}CuN_3O$, C: 54.81, H: 5.55, N: 13.70, Cu: 20.71%. Found, C: 54.49, H: 5.50, N: 13.21, Cu: 20.93%.

A very thin plate of hexagonal shape with dimensions $0.45 \times 0.45 \times 0.08$ mm was mounted on a glass fiber with epoxy resin. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf–Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method using monochromatized radiation in the range $2 < \theta < 20°$; as the crystal was very thin it did not diffract at all beyond 20° in θ. The intensities of two reflections, chosen as standards, were monitored at 2 h intervals of exposure time and decreased in a linear fashion by 0.5% over the course of the data collection; this decay was corrected for by appropriate scaling. Intensities of 1280 independent reflections (h 0–7, k 0–19, l 0–19) were measured using