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# (Benzoylacetonato-*O*,*O*′)(2,2′-bipyridine-*N*,*N*′)(nitrato-*O*)copper(II)

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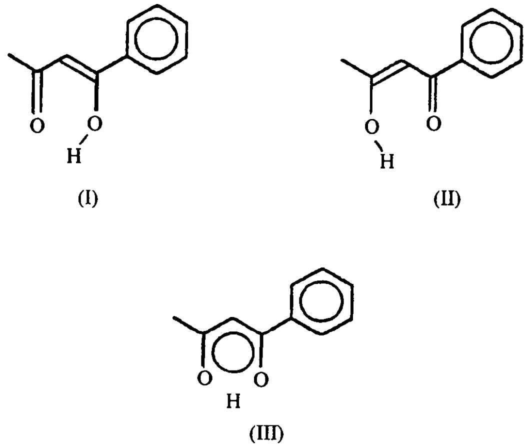
## Abstract

The Cu$^{II}$ atom in the title complex, (2,2′-bipyridine-*N*,*N*′)(nitrato-*O*)(1-phenyl-1,3-butanedionato-*O*,*O*′)copper(II), [Cu($C_{10}H_9O_2$)($NO_3$)($C_{10}H_8N_2$)], has a square-pyramidal coordination. Both the benzoylacetone anion and the 2,2′-bipyridine ligand chelate to the Cu$^{II}$ atom in the equatorial plane, while a nitrate anion occupies the apical site, with a longer Cu—O distance of 2.335 (4) Å. Within the delocalized enol ring of benzoylacetone, the C—C bond closest to the phenyl ring is longer than the C—C bond farthest from the phenyl ring.

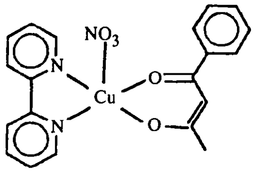
## Comment

The keto–enol tautomerism of 1,3-diketones has been extensively studied. For asymmetric benzoylacetone, enolization brings about two forms of *cis*-enol [forms (I) and (II)] which alternate quickly in solution *via* form (III), as shown in the scheme below (Gorodetsky, Luz & Mazur, 1967).



(I) (II) (III)

An NMR study suggested that form (I) dominates in solution (Winter, Zeller & Berger, 1979), while a neutron-diffraction study (Jones, 1976) and an accurate low-temperature X-ray study (Winter, Zeller & Berger, 1979) indicated that within the delocalized enol ring, the C—C bond farthest from the phenyl ring is slightly longer than the C—C bond closest to the phenyl ring. The structure of the title complex, [Cu(bzac)(bipy)($NO_3$)] (where bzac is benzoylacetonate and bipy is 2,2′-bipyridine), (1), however, shows that the C—C bond close to the phenyl ring is longer when benzoylacetone chelates to a metal atom.



(1)

The Cu$^{II}$ atom has a square-pyramidal coordination, as shown in Fig. 1. A benzoylacetone anion and a 2,2′-bipyridine molecule chelate to the Cu$^{II}$ atom in the equatorial plane, with an average Cu—O distance of 1.911 (3) Å and an average Cu—N distance of 1.985 (3) Å. A nitrate anion occupies the apical site, the Cu—O3 distance of 2.335 (4) Å being about 0.4 Å longer than the Cu—O distance in the equatorial plane. Both the enol ring (defined by atoms Cu, O1, O2, C2, C3 and C4) and the 2,2′-bipyridine ligand are highly coplanar with the Cu$^{II}$ atom, but these planes are inclined with respect to one another like an umbrella, the dihedral angle being 13.4°. The Cu$^{II}$ atom deviates by about 0.15 Å from the mean plane defined by atoms O1, O2, N1 and N2 towards the apical direction. The C4—C5 distance of 1.494 (6) Å suggests that this bond is a single bond and the phenyl ring of the benzoylacetone anion may freely rotate around it in solution. In the solid state, the dihedral angle between the phenyl and enol rings may depend on van der Waals contacts between neighbouring molecules. The dihedral angle of 22.9 (1)° for the present complex is different from the dihedral angle of 6° found in the structure of the free benzoylacetone molecule (Jones, 1976). The distance of 3.456 (7) Å between the C10 and C11($-x$, $-y$, $-z$) atoms indicates a van der Waals contact between the phenyl ring and the 2,2′-bipyridine ligand from the neighbouring molecule.

Within the enol ring of this complex, delocalization of the double bond is observed as reported for the free benzoylacetone molecule, but the C2—C3 bond distance of 1.376 (6) Å is significantly shorter than the C3—C4 bond distance of 1.398 (6) Å. This is contrary to the conclusion that resonance form (I) dominates for free benzoylacetone and also contrary to the results of a benzoylacetone–Schiff base complex

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† On leave from the Hangzhou Institute of Commerce as a visiting scholar.

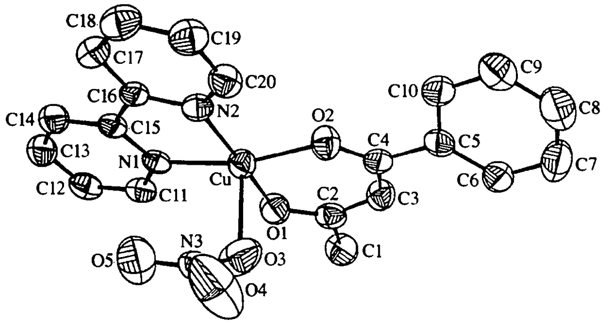

Fig. 1. The molecular structure of [Cu(bzac)(bipy)(NO$_3$)] showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

reported previously, where the C—C bond farthest from the phenyl ring is longer than the C—C bond closest to it (Xu, Chen, Chen, Miki & Kasai, 1989).

The crystal of (1) consists of discrete complex molecules. The shortest intermolecular non-bonded contact distance of 3.318 (6) Å is between the C5 and C11($-x$, $-y$, $-z$) atoms.

## Experimental

Benzoylacetone (1 mmol) and 2,2′-bipyridine (1 mmol) were dissolved in 10 ml ethanol. The resulting solution was dropped into 10 ml of ethanol solution containing Cu(NO$_3$)$_2$ (1 mmol) with continuous stirring at room temperature. The dark green crystals were obtained after standing for several days.

*Crystal data*

[Cu(C$_{10}$H$_9$O$_2$)(NO$_3$)(C$_{10}$H$_8$N$_2$)]
$M_r$ = 442.92
Monoclinic
$P2_1/n$
$a$ = 10.471 (3) Å
$b$ = 14.347 (2) Å
$c$ = 13.290 (3) Å
$\beta$ = 111.65 (2)°
$V$ = 1855.6 (8) Å$^3$
$Z$ = 4
$D_x$ = 1.59 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 25 reflections
$\theta$ = 10.6–13.8°
$\mu$ = 1.215 mm$^{-1}$
$T$ = 296 K
Prism
0.45 × 0.38 × 0.22 mm
Dark green

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* $\psi$ scans (*TEXSAN*; Molecular Structure Corporation, 1989)
$T_{\min}$ = 0.525, $T_{\max}$ = 0.765
3607 measured reflections
3421 independent reflections

2269 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.018
$\theta_{\max}$ = 25°
$h = -6 \rightarrow 12$
$k = -16 \rightarrow 17$
$l = -15 \rightarrow 14$
3 standard reflections every 300 reflections intensity decay: 3.4%

*Refinement*

Refinement on $F$
$R$ = 0.043
$wR$ = 0.049
$S$ = 1.23
2269 reflections
262 parameters
H atoms not refined
Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{\max}$ = 0.06
$\Delta\rho_{\max}$ = 0.39 e Å$^{-3}$
$\Delta\rho_{\min}$ = −0.32 e Å$^{-3}$
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu—O1 | 1.915 (3) | N1—C15 | 1.341 (5) |
| Cu—O2 | 1.907 (3) | N2—C16 | 1.344 (5) |
| Cu—O3 | 2.335 (4) | N2—C20 | 1.334 (5) |
| Cu—N1 | 1.988 (3) | C1—C2 | 1.507 (6) |
| Cu—N2 | 1.982 (3) | C2—C3 | 1.376 (6) |
| O1—C2 | 1.276 (5) | C3—C4 | 1.398 (6) |
| O2—C4 | 1.268 (5) | C4—C5 | 1.494 (6) |
| N1—C11 | 1.336 (5) | C15—C16 | 1.470 (5) |
| O1—Cu—O2 | 93.7 (1) | C11—N1—C15 | 118.8 (4) |
| O1—Cu—O3 | 93.5 (3) | Cu—N2—C16 | 115.2 (3) |
| O1—Cu—N1 | 93.1 (1) | Cu—N2—C20 | 125.8 (3) |
| O1—Cu—N2 | 172.5 (1) | C16—N2—C20 | 119.1 (4) |
| O2—Cu—O3 | 89.4 (3) | O1—C2—C1 | 114.7 (4) |
| O2—Cu—N1 | 165.6 (1) | O1—C2—C3 | 126.4 (4) |
| O2—Cu—N2 | 91.1 (1) | C1—C2—C3 | 118.9 (4) |
| O3—Cu—N1 | 102.9 (5) | C2—C3—C4 | 124.3 (4) |
| O3—Cu—N2 | 92.4 (4) | O2—C4—C3 | 124.4 (4) |
| N1—Cu—N2 | 81.0 (1) | O2—C4—C5 | 114.7 (4) |
| Cu—O1—C2 | 124.6 (3) | C3—C4—C5 | 120.9 (4) |
| Cu—O2—C4 | 126.4 (3) | C4—C5—C6 | 122.5 (4) |
| Cu—N1—C11 | 126.1 (3) | C4—C5—C10 | 119.0 (4) |
| Cu—N1—C15 | 115.0 (3) | | |

The title structure was solved by direct methods and refined anisotropically for all non-H atoms by full-matrix least squares. The H-atom sites were obtained from a difference Fourier map and not refined. All computations were performed on a MicroVAX 3100 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1108). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (Acetonitrile-*N*)($\eta^5$-cyclopentadienyl)bis(triphenylphosphine-*P*)ruthenium(II) Tetrafluoroborate

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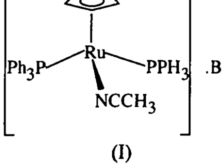
## Abstract

The title compound, $[Ru(C_5H_5)(CH_3CN)\{(C_6H_5)_3P\}_2]$-$BF_4$, crystallizes with $C_1$ local point group symmetry. The Ru—P distances are 2.343 (1) and 2.365 (1) Å, and the Ru—N—C angle is 169.8 (5)°.

## Comment

While investigating the reactivity of $[Ru(Cp)\{(C_6H_5)_3P\}_2(CH_3CN)]^+$ (Cp is cyclopentadienyl), we obtained single crystals of its tetrafluoroborate salt, (I). A search of the literature yielded few structurally characterized acetonitrile–Ru derivatives (Crocker, Green, Orpen & Thomas, 1984; Crocker *et al.*, 1987; Luginbühl *et al.*, 1991; McCormick, Cox & Gleason, 1993; Kirchner, Taube, Scot & Willett, 1993), which prompted us to carry out the present crystal structure determination.



(I)

The title Ru complex does not exhibit mirror symmetry. The angles around the Ru atom are P1—Ru—N1 89.8 (1), P2—Ru—N1 92.2 (1), P1—Ru—P2 101.16 (3), *Cp*—Ru—P1 124.0, *Cp*—Ru—P2 120.4 and *Cp*—Ru—N1 121.3° (where *Cp* is the Cp centroid). The average distance from the Ru atom to the C atoms of the Cp ligand is 2.206 Å, while the Ru—*Cp* distance is 1.848 Å and the average C—C bond length in the Cp ligand is 1.416 Å. The Ru—N—C6 angle is 169.8 (5)°, showing a significant deviation from perfect linear coordination. The Ru—P distances are significatively different, albeit $^{31}P$ NMR shows one signal only at 42.48 p.p.m. ($CD_2Cl_2$ solution). The overall slight dissymmetry of the complex is reminiscent of the situation found in $[Ru(Cp)\{(C_6H_5)_4C_4\}(CH_3CN)]^+$ (Crocker *et al.*, 1984), who ascribe the asymmetric coordination of the $(C_6H_5)_4C_4$ ligand to the metal centre to the nature of the frontier orbitals of the Cp–Ru(MeCN)$^+$ fragment. Also noteworthy are the high displacement parameters of the acetonitrile group likening it to a weakly bound pendulum. This, in fact, is an 'X-ray photograph' of the leaving group character of the acetonitrile ligand.

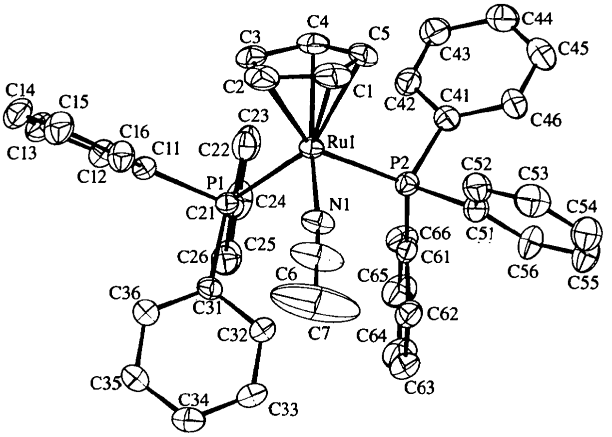


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.

## Experimental

The synthesis of (I) was carried out by stirring stoichiometric amounts of $[Ru(Cp)\{(C_6H_5)_3P\}_2Cl]$ (Bruce, Hamester, Swincer & Wallis, 1982) with $AgBF_4$ in acetonitrile at room temperature overnight. After filtering out AgCl, the solution was evaporated to dryness and the yellow solid recrystallized from $CH_2Cl_2$–heptane (1:5). Single crystals were obtained by slow evaporation of a degassed toluene–$CH_2Cl_2$ (1:1) solution under an inert atmosphere over a period of 15 d.

### *Crystal data*

$[Ru(C_5H_5)(C_2H_3N)$-$(C_{18}H_{15}P)_2]BF_4$
$M_r = 818.60$
Monoclinic
$P2_1/c$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 11$–$12°$

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