# Variable Coordination and Conformation of the 3-Cyano-2,4-pentanedionato Anion in a Mixed-Ligand Binuclear Copper(II) Chelate

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The addition of dipyridylamine to bis(3-cyano-2,4-pentanedionato)copper(II), Cu(NC-acac)$_2$, induces changes in the mode of interaction and the conformation of the NC-acac$^-$ anion. The structure of the resulting binuclear compound was determined from a single microcrystal (monoclinic, space group $P2_1$, $a = 7.894(7)$ Å, $b = 25.550(24)$ Å, $c = 11.661(13)$ Å, $\beta = 106.10(8)°$, $Z = 2$, $R_1 = 0.0564$, $_wR_2 = 0.1197$). In the addition compound {[Cu(NC-acac)dipyamH](NC-acac)}$_2$ when the NC-acac$^-$ acts as a chelating and bridging ligand, it assumes the commonly observed *U*(*Z*,*Z*) conformation, while behavior as weakly N-coordinated unidentate counteranion imposes the rarely encountered *S*(*Z*,*E*) conformation. In the [Cu(NC-acac)dipyamH](NC-acac)] entities one of the copper(II) centers is a 4 + 2 Jahn−Teller complex while the other is a square-based pyramid.

## Introduction

The exceptional properties of the metal chelates of $\beta$-diones[1−7] have stimulated research in these interesting compounds that find a variety of laboratory uses and many industrial applications.[5−7] Alkyl and aryl substituents influence distinctive physicochemical properties by engendering stereoelectronic effects, the nature and intensity of which depends on their proximity to the carbonyl carbon atoms. Furthermore, the ligated anions of the prototropic $\beta$-diones are susceptible to electrophilic attack, and in addition to hydrocarbon derivatives that may induce steric pressure and alter the conformation,[8] other groups are easily attached to the *para* position of the chelate ring.[1] Substituents with terminal donor atoms, such as the cyano, thiocyano, and nitro groups, are of particular importance since they are capable of interacting covalently with coordinatively unsaturated metal centers.[9,10] These interactions affect the thermal stability and volatility of the metal $\beta$-dionates that make them important precursors in the production of high-temperature superconductors by metal-organic chemical vapor deposition (MOCVD) techniques.[7] In the prototropic $\beta$-diones and their monoanions ($\beta^-$), because of hydrogen bonding and chelate formation through the carbonyl oxygens, the *U*(*Z*,*Z*) conformation predominates.[2,3] It persits even in cases in which $\beta^-$ acts as weakly coordinating counteranion.[11] However the $\beta$-diketones and their anions interact with metal ions electrostatically or covalently in a variety of modes[2] and are capable of attaining various conformations and configurations,[3] the study of which so far has been the province of theoretical chemistry.[12] Until recently neither the influence of functional groups nor the interactions with metal ions have been advantageously exploited to induce changes in conformation of a $\beta$-dione even though they provide geometric shapes that endow the metal chelates with special magnetic and electronic properties.[5] Compounds in which a $\beta$-dione attains more than one conformation have eluded isolation. Lately we indicated that attachment of the cyano group to the methinic carbon atom of 2,4-pentanedione has important repercussions on the mode of interaction and the conformation of its monoanion, NC-acac$^-$.[13] Actually, while the Cu$\beta_2$ chelates react with uni- and bidentate nitrogenous bases and the composition of the resulting addition compounds depends on the concentration and structure of the reactants,[14] in the reaction of Cu(NC-acac)$_2$ with partially N-substituted 1,2-diamines, enR, the monoadduct is unstable and disproportionates affording Cu(NC-acac)$_2$ and [Cu(enR)$_2$-(NC-acac)$_2$]. In the later compound NC-acac$^-$ adopts the *S*(*E*,*Z*) conformation and acts as a weakly coordinating counteranion.[13]

In an endeavor to extent the range of metal chelates in which the anion of a $\beta$-dione attains a conformation other than the usually encountered *U*(*Z*,*Z*), we report the first synthesis of a copper(II) chelate, {[Cu(NC-acac)dipyamH](NC-acac)}$_2$ (dipyamH denotes 2,2′-dipyridylamine), in which the $\beta$-dione exhibits variable denticity and conformation and the copper(II) cation different coordination numbers along with its crystal structure and some physicochemical properties.

## Experimental Section

**Preparation and Characterization of {[Cu(NC-acac)dipyamH]-(NC-acac)}$_2$.** The synthesis of bis(3-cyano-2,4-pentanedionato)copper-(II), Cu(NC-acac)$_2$, was achieved by Fackler's method.[13] The addition

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**Table 1.** Crystal Data and Experimental Details for the Structural Study of {[Cu(NC-acac)dipyamH](NC-acac)}$_2$

| | |
|---|---|
| formula | $C_{44}H_{42}N_{10}O_8Cu_2$ |
| molecular mass, $M_r$ | 965.97 |
| **Crystal Parameters** | |
| cryst shape | pale green rectangular prisms |
| cryst size (mm$^3$) | 0.28 × 0.35 × 0.23 |
| cryst system | monoclinic |
| space group | $P2_1$ |
| unit-cell dimens | |
| $a$ (Å) | 7.894(7) |
| $b$ (Å) | 25.550(24) |
| $c$ (Å) | 11.661(13) |
| α (deg) | 90 |
| $\beta$ (deg) | 106.10(8) |
| $\gamma$ (deg) | 90 |
| $V_c$ (Å$^3$) | 2259.6(4) |
| molecules per cell, Z | 2 |
| $D_x$ (Mg m$^{-3}$) | 1.42 (calcd) |
| **Measurement of Intensity Data** | |
| instrument | PW1100-STOE |
| radiation | Mo Kα, $\lambda = 0.710\ 69$ Å |
| monochromator | graphite |
| scan mode | $\omega/2\theta$ |
| $\omega$ range | 2.0−30.0 |
| no. of reflcns measd | 9659 |
| no. of independent reflcns | 7253 |
| no. of reflcns obsd | 3802 reflected [$I \geq 2\sigma(I)$] |
| indices limits | |
| h | −2 to +11 |
| k | −2 to +35 |
| l | −16 to +16 |
| $F$(000) | 996 |
| no. of reflcns for cell meas | 25 with 20° ≤ $\theta$ ≤ 25° |
| no. of params refined | 586 |
| linear abs coeff, $\mu$ (cm$^{-1}$) | 10.45 |
| **Final Discrepancy Factors**[a] | |
| $R_1 = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$ | 0.0564 |
| $_wR_2 = [\sum w(\lvert F_o^2\rvert - \lvert F_c^2\rvert)^2/\sum w(\lvert F_o^4\rvert)]^{1/2}$ | 0.1197 |

[a] $w = [\sigma^2(F_o^2) + (0.0382P)^2 + 0.39P]^{-1}$ ($P = [\max(F_o^2,0) + 2F_o^2]/3$).

**Table 2.** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for the Non-Hydrogen Atoms of {[Cu(CN-acac)dipyamH](CN-acac)}$_2$ with Esd's in Parentheses

| atom | x | y | z | $U$(eq)[a] |
|---|---|---|---|---|
| Cu(A) | 5467(1) | 6609(1) | 9170(1) | 40(1) |
| N(3A) | 3144(8) | 6522(3) | 7977(5) | 40(2) |
| C(13A) | 2934(9) | 6309(3) | 6902(5) | 35(2) |
| C(14A) | 1295(11) | 6271(3) | 6065(6) | 46(2) |
| C(15A) | −147(11) | 6459(3) | 6350(8) | 55(2) |
| C(16A) | 23(9) | 6672(4) | 7470(7) | 55(2) |
| C(17A) | 1656(10) | 6692(3) | 8264(7) | 52(2) |
| N(4A) | 6473(7) | 6025(2) | 8454(4) | 34(1) |
| C(18A) | 5891(10) | 5893(3) | 7319(6) | 33(2) |
| C(19A) | 6790(10) | 5531(3) | 6815(7) | 45(2) |
| C(20A) | 8214(11) | 5276(3) | 7512(7) | 48(2) |
| C(21A) | 8773(10) | 5394(3) | 8717(7) | 46(2) |
| C(22A) | 7867(10) | 5773(3) | 9159(6) | 41(2) |
| N(5A) | 4384(8) | 6114(2) | 6596(4) | 39(2) |
| O(2A) | 4619(7) | 7237(2) | 9854(4) | 51(2) |
| C(4A) | 5294(12) | 7415(3) | 10890(7) | 47(2) |
| C(5A) | 4142(12) | 7802(4) | 11313(9) | 70(3) |
| C(3A) | 6978(10) | 7296(3) | 11597(6) | 43(2) |
| C(2A) | 8199(10) | 6998(3) | 11186(6) | 47(2) |
| C(1A) | 10094(10) | 6968(4) | 11929(8) | 69(3) |
| O(1A) | 7841(6) | 6765(2) | 10206(4) | 49(1) |
| C(6A) | 7520(11) | 7493(3) | 12783(7) | 59(2) |
| N(1A) | 7985(10) | 7636(4) | 13749(7) | 85(3) |
| N(2A) | 4577(11) | 6112(3) | 10603(6) | 63(2) |
| C(12A) | 4134(10) | 5903(3) | 11353(7) | 46(2) |
| C(9A) | 3675(9) | 5638(3) | 12280(5) | 34(2) |
| C(10A) | 3008(9) | 5117(3) | 11988(6) | 43(2) |
| O(4A) | 2771(8) | 4938(2) | 10994(5) | 71(2) |
| C(11A) | 2640(11) | 4762(3) | 12937(6) | 56(2) |
| C(8A) | 3974(10) | 5899(3) | 13396(6) | 43(2) |
| O(3A) | 3553(8) | 5720(2) | 14269(4) | 62(2) |
| C(7A) | 4866(12) | 6429(3) | 13543(7) | 62(2) |
| Cu(B) | 5986(1) | 3776(1) | 6363(1) | 37(1) |
| N(3B) | 8198(7) | 3851(3) | 7678(4) | 36(1) |
| C(13B) | 8296(10) | 4034(3) | 8778(6) | 38(2) |
| C(14B) | 9885(11) | 4029(3) | 9663(6) | 57(2) |
| C(15B) | 11376(11) | 3863(4) | 9420(7) | 68(2) |
| C(16B) | 11328(11) | 3694(4) | 8290(7) | 64(2) |
| C(17B) | 9709(10) | 3697(3) | 7452(6) | 47(2) |
| N(4B) | 4827(8) | 4322(2) | 7111(4) | 36(1) |
| C(18B) | 5325(10) | 4447(3) | 8281(6) | 34(2) |
| C(19B) | 4415(10) | 4814(3) | 8765(6) | 40(2) |
| C(20B) | 2974(11) | 5043(3) | 8044(7) | 51(2) |
| C(21B) | 2455(11) | 4938(3) | 6835(7) | 49(2) |
| C(22B) | 3385(10) | 4579(3) | 6408(6) | 43(2) |
| N(5B) | 6833(7) | 4224(2) | 9034(4) | 40(2) |
| O(2B) | 6886(7) | 3128(2) | 5907(4) | 51(1) |
| C(4B) | 6314(11) | 2878(3) | 4965(7) | 44(2) |
| C(5B) | 7507(11) | 2470(3) | 4672(8) | 69(3) |
| C(3B) | 4619(11) | 2947(3) | 4190(6) | 46(2) |
| C(2B) | 3343(11) | 3299(3) | 4403(6) | 49(2) |
| C(1B) | 1496(11) | 3293(4) | 3617(7) | 66(2) |
| O(1B) | 3713(7) | 3624(2) | 5249(4) | 53(2) |
| C(6B) | 4101(11) | 2605(4) | 3159(7) | 57(2) |
| N(1B) | 3736(10) | 2325(4) | 2368(6) | 79(3) |
| N(2B) | 6918(9) | 4248(3) | 5072(5) | 56(2) |
| C(12B) | 7251(10) | 4452(3) | 4291(6) | 43(2) |
| C(9B) | 7679(9) | 4705(3) | 3331(5) | 41(2) |
| C(10B) | 8302(10) | 5236(3) | 3573(6) | 45(2) |
| O(4B) | 8543(9) | 5419(2) | 4574(5) | 72(2) |
| C(11B) | 8680(11) | 5565(3) | 2605(7) | 60(2) |
| C(8B) | 7347(9) | 4426(3) | 2227(6) | 46(2) |
| O(3B) | 7661(8) | 4611(3) | 1318(4) | 69(2) |
| C(7B) | 6539(12) | 3890(4) | 2145(7) | 77(3) |

[a] $U$(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

compound {[Cu(NC-acac)dipyamH](NC-acac)}$_2$ was prepared by dissolving Cu(NC-acac)$_2$ in an inert solvent (e.g. acetonitrile) and adding the required amount of bis(2-pyridyl)amine, dipyamH, also dissolved in the same solvent. Slow evaporation of the solvent under refrigeration allowed the growth of crystals suitable for X-ray analysis (Mp (dec): 176 °C). The stoichiometry of the new copper(II) dimer was determined by elemental analysis. Anal. Calcd: C, 54.71; N, 14.50; H, 4.38; Cu, 13.16. Found: C, 54.6; N, 14.3; H, 4.40; Cu, 13.1. Its molar conductivity ($\Lambda_M = 73$ S m$^2$ mol$^{-1}$ in acetonitrile), the electronic excitation and infrared spectra and its magnetic susceptibility ($\mu_{eff} = 1.43\ \mu_B$) were determined as detailed elsewhere.[13a] The reference compound [Cu(dpamH)NC-acac(H$_2$O)]ClO$_4$ was prepared as described before.[13a]

**X-ray Crystallographic Analysis of {[Cu(NC-acac)dipyamH](NC-acac)}$_2$.** The crystal studied was a rectangular prism and showed to be perfectly stable in the X-ray beam over the period of data acquisition. Intensities of X-ray reflections within two octants of the reciprocal sphere were collected by means of a four-circle Phillips-STOE computer-controlled X-ray diffractometer employing graphite-monochromated Mo Kα radiation. Cell constants and an orientation matrix were obtained by least-squares refinement of the setting angles of 20 randomly selected reflections of high intensity. Accurate unit cell dimensions of the crystal of {[Cu(NC-acac)dipyamH](NC-acac)}$_2$ and an improved orientation matrix were obtained from the least-squares refinement of the setting angles of the 25 strongest independent reflections found between 20.0 and 25.0° in $\theta$. Intensities for the derivation of structural parameters were collected by employing the $\omega/2\theta$ technique. Three standard reflections were monitored periodically to detect intensity changes during the course of the data acquisition. The scale factor determined by these standard reflections was essentially constant, with only an insignificant random variation due to instrument instability. All intensities were corrected as usual for Lorentz and polarization effects. Of the reflections collected, the 3802 that were unique and in compliance with the acceptance criterion $I \geq 2\sigma(I)$, were employed in the analyses. Systematic absences led to space group $P2_1$.

**Table 3.** Selected Interatomic Distances (Å) and Bond Angles (deg) of {[Cu(CN-acac)dipyamH](CN-acac)}$_2$ with Esd's in Parentheses

| | | | | | |
|---|---|---|---|---|---|
| Cu(A)−O(1A) | 1.968(5) | C(3A)−C(6A) | 1.420(10) | N(4B)−C(18B) | 1.349(8) |
| Cu(A)−N(4A) | 1.981(6) | C(2A)−O(1A) | 1.249(8) | N(4B)−C(22B) | 1.371(9) |
| Cu(A)−N(3A) | 1.983(6) | C(2A)−C(1A) | 1.508(10) | C(18B)−N(5B) | 1.391(9) |
| Cu(A)−O(2A) | 1.990(6) | C(6A)−N(1A) | 1.145(9) | C(18B)−C(19B) | 1.392(9) |
| Cu(A)−N(2A) | 2.356(7) | N(2A)−C(12A) | 1.158(9) | C(19B)−C(20B) | 1.347(10) |
| Cu(A)−N(1B) | 2.754(8) | C(12A)−C(9A) | 1.405(10) | C(20B)−C(21B) | 1.380(10) |
| N(3A)−C(13A) | 1.334(8) | C(9A)−C(8A) | 1.422(9) | C(21B)−C(22B) | 1.352(11) |
| N(3A)−C(17A) | 1.378(9) | C(9A)−C(10A) | 1.437(10) | O(2B)−C(4B) | 1.242(8) |
| C(13A)−N(5A) | 1.383(9) | C(10A)−O(4A) | 1.212(8) | C(4B)−C(3B) | 1.403(11) |
| C(13A)−C(14A) | 1.391(10) | C(10A)−C(11A) | 1.519(10) | C(4B)−C(5B) | 1.506(11) |
| C(14A)−C(15A) | 1.359(12) | C(8A)−O(3A) | 1.242(8) | C(3B)−C(2B) | 1.424(11) |
| C(15A)−C(16A) | 1.387(11) | C(8A)−C(7A) | 1.515(11) | C(3B)−C(6B) | 1.450(11) |
| C(16A)−C(17A) | 1.363(10) | Cu(B)−O(2B) | 1.933(5) | C(3B)−N(1B) | 2.589(10) |
| N(4A)−C(18A) | 1.318(8) | Cu(B)−O(1B) | 1.940(6) | C(2B)−O(1B) | 1.259(9) |
| N(4A)−C(22A) | 1.341(8) | Cu(B)−N(3B) | 1.988(6) | C(2B)−C(1B) | 1.491(11) |
| C(18A)−C(19A) | 1.390(10) | Cu(B)−N(4B) | 1.997(6) | C(6B)−N(1B) | 1.139(9) |
| C(19A)−C(20A) | 1.358(10) | Cu(B)−N(2B) | 2.210(6) | N(2B)−C(12B) | 1.141(8) |
| C(20A)−C(21A) | 1.385(10) | N(3B)−C(13B) | 1.346(8) | C(12B)−C(9B) | 1.413(9) |
| C(21A)−C(22A) | 1.384(10) | N(3B)−C(17B) | 1.350(9) | C(9B)−C(8B) | 1.431(10) |
| O(2A)−C(4A) | 1.262(8) | C(13B)−N(5B) | 1.361(9) | C(9B)−C(10B) | 1.442(11) |
| O(2A)−Cu(A) | 1.990(6) | C(13B)−C(14B) | 1.386(10) | C(10B)−O(4B) | 1.223(8) |
| C(4A)−C(3A) | 1.390(11) | C(14B)−C(15B) | 1.353(11) | C(10B)−C(11B) | 1.504(10) |
| C(4A)−C(5A) | 1.516(12) | C(15B)−C(16B) | 1.377(11) | C(8B)−O(3B) | 1.247(8) |
| C(3A)−C(2A) | 1.413(11) | C(16B)−C(17B) | 1.377(10) | C(8B)−C(7B) | 1.502(12) |

| | | | | | |
|---|---|---|---|---|---|
| O(1A)−Cu(A)−N(4A) | 89.3(2) | C(3A)−C(4A)−C(5A) | 120.7(7) | N(3B)−C(17B)−C(16B) | 124.0(6) |
| O(1A)−Cu(A)−N(3A) | 172.3(2) | C(4A)−C(3A)−C(2A) | 123.2(7) | C(18B)−N(4B)−C(22B) | 116.8(6) |
| N(4A)−Cu(A)−N(3A) | 91.2(3) | C(4A)−C(3A)−C(6A) | 118.7(8) | C(18B)−N(4B)−Cu(B) | 124.5(5) |
| O(1A)−Cu(A)−O(2A) | 87.7(2) | C(2A)−C(3A)−C(6A) | 118.1(7) | C(22B)−N(4B)−Cu(B) | 118.6(4) |
| N(4A)−Cu(A)−O(2A) | 174.8(2) | O(1A)−C(2A)−C(3A) | 124.4(7) | N(4B)−C(18B)−N(5B) | 120.0(6) |
| N(3A)−Cu(A)−O(2A) | 91.3(3) | O(1A)−C(2A)−C(1A) | 115.9(7) | N(4B)−C(18B)−C(19B) | 122.1(7) |
| O(1A)−Cu(A)−N(2A) | 95.4(2) | C(3A)−C(2A)−C(1A) | 119.6(7) | N(5B)−C(18B)−C(19B) | 117.9(6) |
| N(4A)−Cu(A)−N(2A) | 97.3(3) | C(2A)−O(1A)−Cu(A) | 126.4(5) | C(20B)−C(19B)−C(18B) | 118.7(7) |
| N(3A)−Cu(A)−N(2A) | 92.2(3) | N(1A)−C(6A)−C(3A) | 177.8(10) | C(19B)−C(20B)−C(21B) | 120.9(8) |
| O(2A)−Cu(A)−N(2A) | 87.2(3) | C(12A)−N(2A)−Cu(A) | 174.8(7) | C(22B)−C(21B)−C(20B) | 118.0(8) |
| O(1A)−Cu(A)−N(1B) | 85.1(2) | N(2A)−C(12A)−C(9A) | 177.3(9) | C(21B)−C(22B)−N(4B) | 123.4(7) |
| N(4A)−Cu(A)−N(1B) | 92.0(3) | C(12A)−C(9A)−C(8A) | 117.7(7) | C(13B)−N(5B)−C(18B) | 129.6(5) |
| N(3A)−Cu(A)−N(1B) | 87.2(2) | C(12A)−C(9A)−C(10A) | 114.8(6) | C(4B)−O(2B)−Cu(B) | 127.7(5) |
| O(2A)−Cu(A)−N(1B) | 83.6(3) | C(8A)−C(9A)−C(10A) | 127.5(6) | O(2B)−C(4B)−C(3B) | 123.6(7) |
| N(2A)−Cu(A)−N(1B) | 170.7(3) | O(4A)−C(10A)−C(9A) | 121.8(7) | O(2B)−C(4B)−C(5B) | 117.3(7) |
| C(13A)−N(3A)−C(17A) | 117.6(6) | O(4A)−C(10A)−C(11A) | 117.4(7) | C(3B)−C(4B)−C(5B) | 119.0(7) |
| C(13A)−N(3A)−Cu(A) | 123.7(5) | C(9A)−C(10A)−C(11A) | 120.8(6) | C(4B)−C(3B)−C(2B) | 124.2(7) |
| C(17A)−N(3A)−Cu(A) | 118.7(5) | O(3A)−C(8A)−C(9A) | 124.2(7) | C(4B)−C(3B)−C(6B) | 117.3(8) |
| N(3A)−C(13A)−N(5A) | 119.6(6) | O(3A)−C(8A)−C(7A) | 117.3(7) | C(2B)−C(3B)−C(6B) | 118.4(7) |
| N(3A)−C(13A)−C(14A) | 122.5(7) | C(9A)−C(8A)−C(7A) | 118.5(6) | C(4B)−C(3B)−N(1B) | 116.3(6) |
| N(5A)−C(13A)−C(14A) | 117.9(6) | O(2B)−Cu(B)−O(1B) | 89.2(2) | C(2B)−C(3B)−N(1B) | 119.3(6) |
| C(15A)−C(14A)−C(13A) | 118.9(7) | O(2B)−Cu(B)−N(3B) | 89.1(2) | O(1B)−C(2B)−C(3B) | 122.1(7) |
| C(14A)−C(15A)−C(16A) | 120.0(7) | O(1B)−Cu(B)−N(3B) | 170.8(2) | O(1B)−C(2B)−C(1B) | 117.6(8) |
| C(17A)−C(16A)−C(15A) | 118.7(8) | O(2B)−Cu(B)−N(4B) | 165.1(2) | C(3B)−C(2B)−C(1B) | 120.3(7) |
| C(16A)−C(17A)−N(3A) | 122.2(7) | O(1B)−Cu(B)−N(4B) | 89.0(2) | C(2B)−O(1B)−Cu(B) | 128.8(6) |
| C(18A)−N(4A)−C(22A) | 119.4(6) | N(3B)−Cu(B)−N(4B) | 90.4(2) | N(1B)−C(6B)−C(3B) | 177.8(10) |
| C(18A)−N(4A)−Cu(A) | 123.2(5) | O(2B)−Cu(B)−N(2B) | 93.6(3) | C(6B)−N(1B)−Cu(A) | 153.1(7) |
| C(22A)−N(4A)−Cu(A) | 117.4(4) | O(1B)−Cu(B)−N(2B) | 94.2(2) | C(3B)−N(1B)−Cu(A) | 152.1(4) |
| N(4A)−C(18A)−N(5A) | 120.8(6) | N(3B)−Cu(B)−N(2B) | 94.9(3) | C(12B)−N(2B)−Cu(B) | 170.8(6) |
| N(4A)−C(18A)−C(19A) | 121.2(7) | N(4B)−Cu(B)−N(2B) | 101.2(3) | N(2B)−C(12B)−C(9B) | 179.4(8) |
| N(5A)−C(18A)−C(19A) | 118.1(6) | C(13B)−N(3B)−C(17B) | 117.8(6) | C(12B)−C(9B)−C(8B) | 117.3(7) |
| C(20A)−C(19A)−C(18A) | 120.1(7) | C(13B)−N(3B)−Cu(B) | 125.0(5) | C(12B)−C(9B)−C(10B) | 114.7(6) |
| C(19A)−C(20A)−C(21A) | 118.6(7) | C(17B)−N(3B)−Cu(B) | 117.1(4) | C(8B)−C(9B)−C(10B) | 127.8(6) |
| C(22A)−C(21A)−C(20A) | 118.6(7) | N(3B)−C(13B)−N(5B) | 120.4(6) | O(4B)−C(10B)−C(9B) | 120.1(7) |
| N(4A)−C(22A)−C(21A) | 121.9(7) | N(3B)−C(13B)−C(14B) | 120.5(7) | O(4B)−C(10B)−C(11B) | 119.4(7) |
| C(18A)−N(5A)−C(13A) | 128.8(5) | N(5B)−C(13B)−C(14B) | 119.2(6) | C(9B)−C(10B)−C(11B) | 120.5(6) |
| C(4A)−O(2A)−Cu(A) | 125.1(5) | C(15B)−C(14B)−C(13B) | 120.5(7) | O(3B)−C(8B)−C(9B) | 123.1(8) |
| O(2A)−C(4A)−C(3A) | 124.7(7) | C(14B)−C(15B)−C(16B) | 120.2(7) | O(3B)−C(8B)−C(7B) | 118.2(7) |
| O(2A)−C(4A)−C(5A) | 114.5(8) | C(17B)−C(16B)−C(15B) | 116.9(8) | C(9B)−C(8B)−C(7B) | 118.7(7) |

Details of crystal analysis, data collection, and structure refinement are given in Table 1, together with the final values for the unit cell.

The copper positions were deduced by direct methods employing the SHELXS-86 program[15] and used to compute a first-approximation electron-density synthesis, which revealed the position of all remaining atoms except the hydrogens. After least-squares refinements with the non-hydrogen atoms, the hydrogen atoms were positioned geometrically (even though their coordinates were determined) and their positions in the difference Fourier map were recalculated after each refinement cycle. All subsequent calculations were performed using the SHELX-93 program.[16] The relative atomic coordinates are listed in Table 2. The figure of the clinographic projection were produced with the ATOMS program.[17] Refinement was carried out by full-matrix least-squares methods, with a weighting factor applied to all reflections. Final $\Delta(\rho)_{max}/\Delta(\rho)_{min} = +0.37/-0.35$ e Å$^{-3}$. Agreement factors are defined

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(15) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(16) Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.

(17) Dowtry, T. *ATOMS* (Version 3.2). *A program for Structure Determination*; Shape Software: Kingsport, 1995.

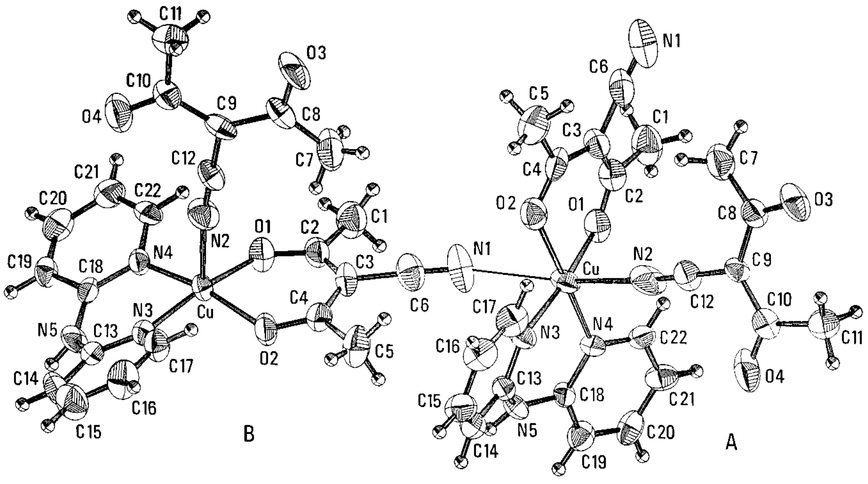

**Figure 1.** Clinographic projection and labeling scheme of the compound $\{[Cu(NC\text{-}acac)dipyamH](NC\text{-}acac)\}_2$ with thermal ellipsoids at the 50% probability level.

as $R_1$ and ${}_{w}R_2$ (Table 1). Further experimental details are deposited with the Cambridge Crystallographic Data Centre.

## Results and Discussion

The reaction of $Cu(NC\text{-}acac)_2$ with bis(2-pyridyl)amine, dipyamH, affords a product with stoichiometry indicative of monoadduct, irrespective of the concentration of the cross-conjugated nitrogenous base. Other bis($\beta$-dionato)copper(II) chelates, $Cu\beta_2$, that have electron-attracting substituents in the cyclometalated ring also afford only the 1:1 adduct when reacted with α-diimines, $N\frown N$.[18] However, there are distinct differences in the bonding characteristics and structure of the products. The $[Cu\beta_2N\frown N]$ adducts exhibit distorted octahedral structure and the Cu−O bond adjacent to the electron-withdrawing group is so much weakened that each becomes one of the two long bonds to the copper rather than the newly formed Cu−N bonds. The addition of dpamH to $Cu(NC\text{-}acac)_2$ is reminiscent of the behavior of $Cu(NC\text{-}acac)_2$ and $Cu\beta_2$ toward partially substituted 1,2-diamines, enR. In the 1:2 addition products the newly formed Cu−N bonds are exceedingly strong and the lengthening of the Cu−O results in bond rupture so that the $\beta$-dionate anion, $\beta^-$, interacts weakly as unidentate ligand. Indications of the weakening and rupture of the Cu−O bonds are gathered from the enhancement in the electrical conductivity of the solutions. Further indications are obtained from the IR bands originating from the stretching vibrations of the perturbed $C\overset{\cdot\cdot}{-}O$ bond of the $\beta$-dionato ligand and especially from the changes in the frequency of the stretching vibrations of the cyano group.

In the IR spectra of the adduct the band due to the perturbed $C\overset{\cdot\cdot}{-}O$ bond is observed at 1616 $cm^{-1}$ while in $Cu(NC\text{-}acac)_2$ appears at 1598 $cm^{-1}$. It probably incorporates the peak emanating from the conjugated $C\overset{\cdot\cdot}{-}N$ bond that in the free nitrogenous base occurs at 1605 $cm^{-1}$. In $Cu(dpamH)Cl_2$ the frequency of this vibration is shifted to 1635 $cm^{-1}$ and in the IR spectra of $[Cu(dipyamH)NC\text{-}acac(H_2O)]ClO_4$ the peak is clearly discernible at 1632 $cm^{-1}$. More informative are the frequencies of the stretching vibration of the cyano group. In the IR spectra of $Cu(NC\text{-}acac)_2$ and $[Cu(dipyamH)NC\text{-}acac(H_2O)]ClO_4$ this is observed as a narrow band at 2210 and 2208 $cm^{-1}$, respectively. In the adduct the band is broader with peaks at 2205, 2197, and 2187 $cm^{-1}$. While the high frequency peak indicates that the $NC\text{-}acac^-$ is O,O ligated, the last two peaks suggest the possibility of enhanced copper−nitrogen interactions with the low-frequency peak implicating action of $NC\text{-}acac^-$ as unidentate ligand. The latter is in accord with results of the addition compounds $[Cu(enR)_2(NC\text{-}acac)_2]$ in which frequencies lower than 2190 $cm^{-1}$ reveal coordination of $NC\text{-}acac^-$ as nitrile and change in the conformation of the $\beta$-dione.[13] Irrefutable proof of the simultaneous existence of $NC\text{-}acac^-$ in two different conformations and unusual interactions with copper(II) was accrued from an X-ray diffraction study.

In the unit cell of the compound $\{[Cu(NC\text{-}acac)dipyamH](NC\text{-}acac)\}_2$ there are four copper atoms. Each metal center has in its immediate vicinity ($r \leq 1.98$ Å) the $sp^2$ hybridized nitrogen atoms of the cross-conjugated nitrogenous base and the oxygen atoms of a $NC\text{-}acac^-$ anion. These four atoms form a plane, and copper is slightly above it. The $N(sp^2)\cdots N(sp^2)$ and $O(1)\cdots O(2)$ intraligand distances of 2.827(4) and 2.720(4) Å, respectively, indicate formation of six-membered metallocyclic rings. The carbon atoms of the cross-conjugated nitrogenous base that are linked via the amino group are symmetricaly disposed and are distanced 0.578 Å from the basal $N_2O_2$ plane. The chelate ring of the nitrogenous base assumes the *boat* conformation as has been observed previously in pseudotetrahedral copper(II) chelates of dpamH and its derivatives.[19] The pyridyl rings form a dihedral angle of 152(±1)°. The $\beta$-dionato chelate ring attains a *half-chair* conformation with copper(II) distanced 0.55 Å from the plane defined by the carbonyl groups and the sceletal carbon atom of the chelated anion. The interatomic distances and bond angles within this moiety (Table 3) are in accord with values reported in the literature for this ligand in the $U(Z,Z)$ conformation.[9]

Charge neutralization is effected by another $NC\text{-}acac^-$ anion interacting with copper through the nitrogen of the cyano group. The Cu−N(sp) distance is appreciably longer than the other Cu−N bonds ($r \geq 2.21$ Å) and the length of this bond was found to vary. This and other small but discernible differences help to discriminate the copper atoms in the $[Cu(NC\text{-}acac)dipyamH](NC\text{-}acac)]$ entities into A and B. In entity A the vector of the Cu−N(sp) bond forms an angle of 5.28° with the normal to the $N_2O_2$ plane. In the unidentate $NC\text{-}acac^-$ anion the intraligand C(7)−C(11) distance of 4.59 Å is shorter than the distance of 5.03 Å separating the C(1) and C(5) methyl groups in the chelated $\beta$-dionato anion displaying the $U(Z,Z)$ conformation. The O(3)−O(4) separation distance of 4.207 Å reaffirms that the unidentate anion adopts the $S(E,Z)$ conformation (Figure 1). The unidentate $NC\text{-}acac^-$ anion is essentially

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(18) Graddon, D. P.; Ong, W. K. *J. Inorg. Nucl. Chem.* **1975**, *37*, 469.

(19) (a) Johnson, J. E.; Beineke, T. A.; Jacobsen, R. A. *J. Chem. Soc. A* **1967**, 1371. (b) Baxter, C. E.; Rodig, O. R. *Inorg. Chem.* **1979**, *18*, 1918.

planar and only the methyl carbon atoms are somewhat distanced from the best plane. Interestingly, while this plane in entity A encompasses copper, in entity B the metal atom is outside the best plane.

The adoption of the *S*(*E*,*Z*) conformation diminishes the separation distance of the C(11) and O(3) atoms to 2.860 Å. The distance separating the symmetrical C(17) and C(22) atoms from the copper-bonded oxygen atoms O(2) and O(1) is in both cases similar (2.846 and 2.837 Å, respectively), and raises the possibility of formation of weak hydrogen bonds.[3] The spatial arrangement of the B entities implicates hydrogen bonding. The orientation and sequence of these entities is such that the O(3B)···N(5B*) separation distance is only 2.746(7) Å and the O(3B)···H···N(5B*) angle is 140.4°.

The basal $N_2O_2$ (Cu(B)) plane is perpendicular to the Cu(A)$N_2O_2$ plane and it is so oriented that the N(1B) of the cyano group lies along the axis connecting Cu(A) and N(2A). The Cu(A)−N(1B) distance is 2.758(10) Å. Given the ability of NC-acac$^-$ to act as a bridging ligand, the relatively low value of molar conductivity and the disparity in the Cu−N(NC) bond lengths, the possibility of weak covalent interactions involving Cu(A) and N(1B) cannot be disregarded. Because no other cyano nitrogen atom is to be found in the proximity of Cu(B) at a distance shorter than 4 Å, the discrepancies in bond lengths and bond angles (Figure 1) that apparently are due to the interactions involving the Cu(A) and N(1B) atoms suggest that the two interacting [Cu(NC-acac)dipyamH](NC-acac) entities constitute a binuclear mixed-ligand compound. Attemps to assign the molecule to a different space group were in discord with the data. Hence, while entity A is a 4 + 2 Jahn−Teller case, entity B is a 4 + 1 square pyramidal compound.

This is the first case of a binuclear copper(II) mixed-ligand chelate in which the anion of a substituted $\beta$-dione, NC-acac$^-$, exhibits variable conformation and denticity acting as *U*(*Z*,*Z*) chelated ligand, as O,O-chelated and N-bridging ligand and as weakly N-coordinating counteranion in the *S*(*Z*,*E*) conformation.

**Supporting Information Available:** Tables of hydrogen atom coordinates, thermal parameters, and complete interatomic distances and bond angles for {[Cu(NC-acac)dipyamH](NC-acac)}$_2$ and a figure showing the unit cell (10 pages). Ordering information is given on any current masthead page.

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