

Synthesis and structure of aqua-2',2'''-(2,6-pyridindiyl-diethylidene)dioxamohydrazide-copper(II) hydrate

K. Andjelković,^{a*} I. Ivanović,^a S. R. Niketić,^{a*} B. Prelesnik^{b*}
and V. M. Leovac^c

^a Chemistry Department, Faculty of Science, University of Belgrade, Studentski trg 16, P.O. Box 158, YU-11001 Belgrade, Yugoslavia

^b Institute of Nuclear Sciences Vinča, P.O. Box 522, YU-11001 Belgrade, Yugoslavia

^c Institute of Chemistry, Faculty of Science, University of Novi Sad, Trg D. Obradovića 3, YU-21000 Novi Sad, Yugoslavia

(Received 21 March 1997; accepted 5 June 1997)

Abstract—In a template synthesis from copper(II) acetate, 2,6-diacetylpyridine, and semioxamazine ($\text{NH}_2\text{COCONHNH}_2$), two new copper(II) complexes, $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{Hdapsox})(\text{H}_2\text{O})]\text{ClO}_4$, (where $\text{H}_2\text{dapsox} = 2',2'''-(2,6\text{-pyridindiyl-diethylidene})\text{dioxamohydrazide}$) were obtained and characterized. The structure of the former complex was determined by a single-crystal X-ray analysis. Cu^{II} is located in a square pyramidal environment. The polydentate ligand, dapsox^{2-} , is coordinated in dianionic form, as an unsymmetrical quadridentate planar system forming one six-membered and two five-membered metal-chelate rings. The fifth coordination site is occupied by a water molecule. © 1997 Elsevier Science Ltd

Keywords: copper(II) complexes; 2,6-diacetylpyridine derivative; crystal structure; square-pyramidal geometry; IR spectra.

The products of the condensation reaction of 2,6-diacetylpyridine (DAP) with acyl hydrazides form a very interesting class of ligands. Besides the ability to act as ligands of changeable dentation, they exhibit stereochemical diversity, particularly with respect to coordination numbers and/or geometries observed in coordination with various transition metal ions [1].

These ligands predominately form complexes with the ions of the first transition series having the pentagonal-bipyramidal (PBP) geometries [2] in which they are coordinated as planar quinque-dentates forming four fused five-membered metal-chelate rings. By selection of suitable acyl groups it is possible to introduce additional potential ligand atoms into the ligand system, thus extending its coordinating abilities and furthering the formation of stereochemically intriguing structures.

We have recently [3,4] concentrated our attention on the coordination capabilities of 2',2'''-(2,6-pyridindiyl-diethylidene)dioxamohydrazide (or H_2dapsox) and its singly or doubly deprotonated forms, (Hdapsox^-) and (dapsox^{2-}), respectively.

The ligand itself has 11 potential ligand atoms some of which are mutually exclusive. This, together with the flexibility of both side chains attached to the pyridine ring, creates quite a diversified stereochemistry with respect to the possible coordination modes, which could be summarized as follows. Among the (essentially) planar structures there are three possible geometrical isomers having bilateral symmetry in which either the terminal NH_2 groups, (I), or the carbonyl groups forming five-membered rings, (II), or the carbonyl groups forming six-membered rings, (III), are coordinated. Another three isomers, (IV, V, and VI) originate from the unsymmetrical combinations of side chain conformations of I, II and III. Furthermore, the ligand may coordinate through one of the hydrazine NH groups (forming a six-membered

* Author to whom correspondence should be addressed.

* Deceased July 1996.

ring fused to the pyridine ring), and the terminal carbonyl group, (VII), or the terminal amino group, (VIII). Due to the steric hindrance in this mode of coordination the other side chain may engage only the imino nitrogen which forms a five-membered ring, with the remainder of the side chain in a pendant conformation out of the plane of the chelate ring system. The number of theoretically possible isomers is triplicated due to the possibility for deprotonation of one or both hydrazine NH groups. Finally, in the unsymmetrically coordinated structures (IV–VIII) two different singly deprotonated forms are possible, so that the total number of theoretically possible geometrical isomers add up to 29 (see Scheme 1).

In the previously described Co^{II} complexes, H_2dapsox acts as a planar quinque dentate with either two axial H_2O ligands [4] or one H_2O and one methanol ligand [3] completing the PBP coordination. The PBP structure common to a number of complexes of Schiff base derivatives of DAP was found [3,4] to be invariant to the extent of deprotonation of H_2dapsox .

In this paper we report on two new Cu^{II} complexes of H_2dapsox : $[\text{Cu}(\text{Hdapsox})(\text{H}_2\text{O})]^+$ and $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})]$, in which the ligand is singly and doubly deprotonated, respectively. To our knowledge, none of the previous reports in the literature [1,5–8] considered copper(II) complexes with singly deprotonated form of this type of ligand. Furthermore, Pelizzi and coworkers showed that Cu^{II} complexes with a doubly deprotonated form of the ligand tend to form polynuclear structures, e.g., tetrameric $\{[\text{Cu}_2(\text{dip})\text{Cl}_2]\text{H}_2\text{O}\}_2$ ($\text{H}_2\text{dip} = 2,6\text{-diacetylpyridinebis(picolinoylhydrazone)}$) [5] or dimeric similar complex $[\text{Zn}_2(\text{dapt})_2]$ ($\text{H}_2\text{dapt} = 2,6\text{-diacetylpyridinebis(2-pentylhydrazone)}$) [6].

Our results, however, show that Cu^{II} forms a mononuclear complex, $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})]$, with doubly deprotonated dapsox^{2-} acting as a quadridentate, with the apical H_2O complementing the square-pyramidal coordination in the solid state. An analogous coordination is proposed on the basis of spectral studies for the mononuclear Cu^{II} complex, $[\text{Cu}(\text{Hdapsox})(\text{H}_2\text{O})]\text{ClO}_4$, with singly deprotonated form of the ligand.

Unlike the majority of mononuclear structures containing ligands derived from acyl hydrazones of DAP which coordinate as symmetrical planar quinque dentates [6], the present structure represents a rare example of the unsymmetrical quadridentate coordination of the type VII.

EXPERIMENTAL

Physical measurements

Infrared spectra were recorded in KBr pellets with a Perkin–Elmer model 1726X FT-IR spectrometer. Molar conductivity was determined in 1×10^{-3}

mol/dm^3 DMF solutions at the ambient temperature using a Jenway-4009 digital conductometer.

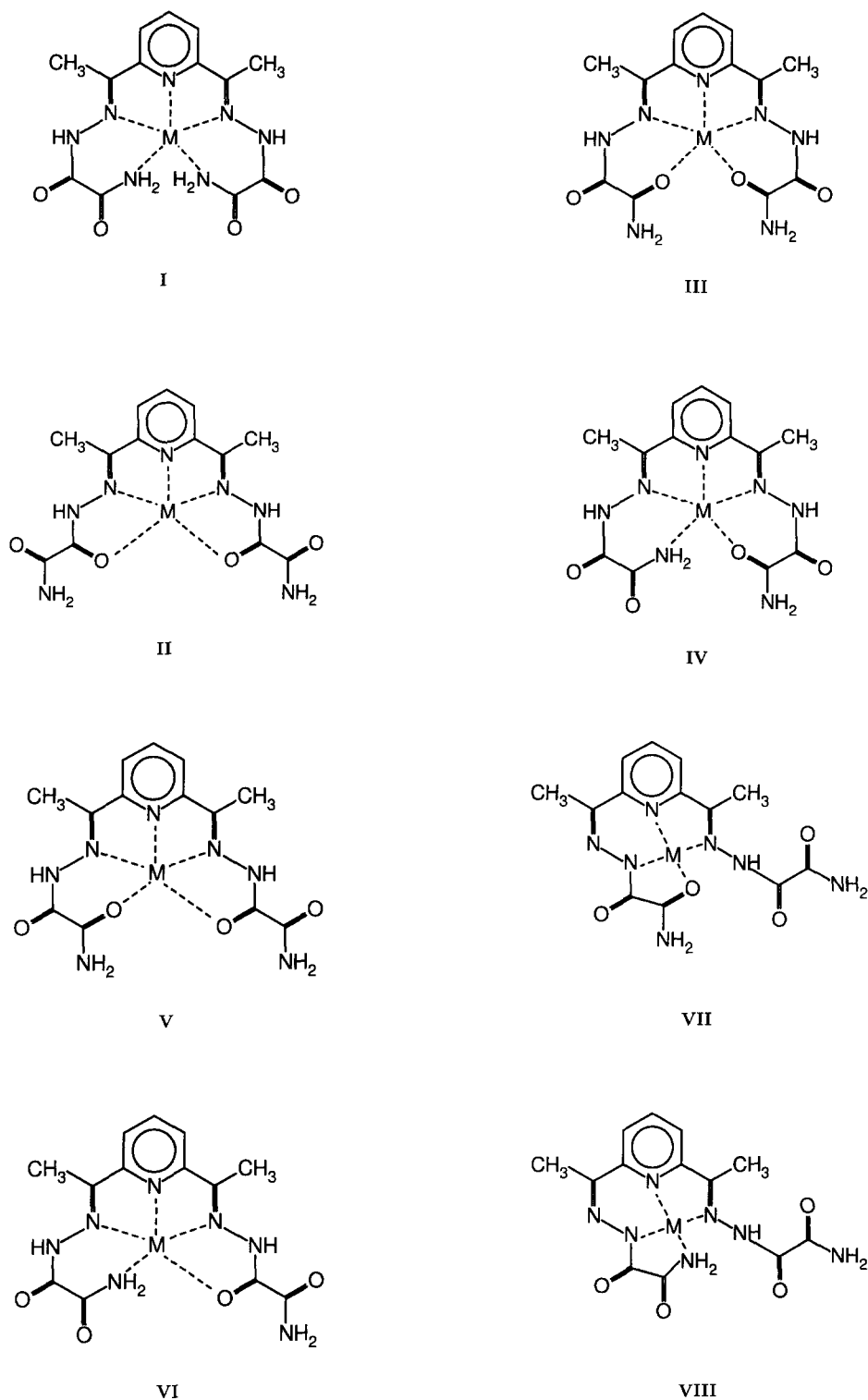
Template syntheses

$[\text{Cu}(\text{dapsox})\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$. Into 25 cm^3 of a mixture of ethanol and water (1 : 1, v/v) 0.20 g (1.2 mmol) of 2,6-diacetylpyridine (DAP), 0.24 g (2.4 mmol) of semioxamazide (SOX), and 0.26 g (1.2 mmol) of copper(II) acetate dihydrate was added. The suspension was heated under reflux until it completely dissolved. The solution was filtered and then left at the ambient temperature for 24 h. The dark green crystalline precipitate was collected by suction filtration and washed with water. Yield : 62%. IR spectrum (KBr; $\bar{\nu}/\text{cm}^{-1}$) : 3478 (s), 3323 (vs), 3270 (vs), 1685 (vs), 1619 (vs), 1582 (vs), 1583 (s), 1455 (s), 1379 (s), 1367 (s), 1331 (m), 1299 (vs), 1272 (vs), 1198 (m), 1161 (m), 1134 (w), 1115 (m), 1103 (s), 995 (w), 926 (w), 878 (w), 817 (w), 710 (m), 686 (m), 670 (m), 659 (m), 577 (m), 563 (m), 519 (w), 463 (w), 425 (w). $\Lambda_{\text{M}} = 3\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Analysis. Found : C 36.6, H 3.5, N 22.8; Calc. for $\text{C}_{13}\text{H}_{17}\text{CuN}_7\text{O}_6$: C 36.2, H 3.9, N 22.7%.

$[\text{Cu}(\text{Hdapsox})(\text{H}_2\text{O})]\text{ClO}_4$. A suspension of 0.20 g (1.2 mmol) of DAP, 0.24 g (2.4 mmol) of SOX, and 0.44 g (1.2 mmol) of copper(II) chlorate hexahydrate in 25 cm^3 of methanol was heated under reflux until it completely dissolved. Shortly after cooling the mixture to ambient temperature, a microcrystalline product started to precipitate. This product was collected by suction filtration and washed with methanol. Yield : 54%. The same product was obtained with the molar ratio of DAP, SOX and Cu^{II} salt of 2 : 2 : 1 or 1 : 1 : 1, as well as with an addition of few drops of HCl (0.1 mol/dm^3) to the reaction mixture. IR spectrum (KBr; $\bar{\nu}/\text{cm}^{-1}$) : 3525 (s), 3458 (s), 3321 (s), 3263 (vs), 3118 (s), 1716 (s), 1684 (vs), 1646 (vs), 1587 (s), 1546 (s), 1510 (s), 1461 (m), 1378 (m), 1332 (w), 1302 (s), 1275 (s), 1224 (m), 1206 (m), 1171 (w), 1143 (m), 1122 (s), 1101 (vs), 948 (w), 932 (w), 834 (w), 810 (m), 754 (w), 733 (w), 717 (m), 657 (w), 626 (m), 584 (w), 520 (w), 495 (w), 481 (w), 422 (w). $\Lambda_{\text{M}} = 63.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Analysis. Found : C 30.2, H 3.0, N 19.1; Calc. for $\text{C}_{13}\text{H}_{16}\text{ClCuN}_7\text{O}_9$: C 30.4, H 3.1, N 19.1%.

Structure determination

A prismatic single crystal (dimensions $0.35 \times 0.30 \times 0.20 \text{ mm}$) of the complex obtained by our template synthesis was mounted on an Enraf–Nonius CAD-4 automated diffractometer equipped with graphite monochromator and Mo anticathode. Unit cell dimensions were obtained from a least-squares refinement of 25 strong reflections with $10 < \theta < 16^\circ$. The $\omega/2\theta$ scan was applied for intensity data measurements and three standard reflections were monitored every hour of exposure time. No changes in the intensities of the standard reflections were observed during the experimental procedure. The data were corrected



Scheme 1.

for Lorentz and polarization effects, but not for absorption. A summary of crystal data and experimental details are listed in Table 1. The phase problem was solved by Patterson synthesis. The structure was refined and completed by a full matrix least-squa-

res method and difference Fourier synthesis, respectively. Hydrogen atoms of H₂O were located in difference Fourier maps and refined isotropically. The other hydrogen atoms were calculated on the basis of geometrical considerations [$d(\text{C}-\text{H}) = d(\text{N}-\text{H}) =$

Table 1. Summary of crystal and experimental data for $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$

Formula	$\text{C}_{13}\text{H}_{17}\text{CuN}_7\text{O}_6$
FW	430.89
Cell type	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	8.1785(13)
b (Å)	10.6175(19)
c (Å)	10.994(2)
α (°)	109.754(17)
β (°)	111.572(15)
γ (°)	97.593(13)
V (Å ³)	798.9(0.5)
Z	2
$F(000)$	442
D_{calc} (g cm ⁻³)	1.804
λ (Mo- K_α) (Å)	0.71073
μ (mm ⁻¹)	1.419
Temperature (K)	294
Scan method	$\omega/2\theta$
θ_{max} (°)	29
Index ranges	$-11 \leq h \leq 11$ $0 \leq k \leq 15$ $-15 \leq l \leq 15$
Number of collected reflections	4498
Number of independent reflections	3912
Number of observed reflections [$I \geq 3\sigma(I)$]	3106
Number of refined parameters	260
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (eÅ ⁻³)	0.65; 0.51
$ \Delta/\sigma _{\text{max}}$	0.02
R	0.039
R_w ($w = [\rho(F_o)]^{-2}$)	0.043
S	0.94

0.95 Å] and they were allowed to ride on the adjacent atom with $B_{\text{H}} = 1.3 \times B_{\text{eq}}$, where B_{eq} is the isotropic equivalent B of the carrier atom. Atomic scattering factors and anomalous-dispersion coefficients were as quoted in SDP [9].

Computational methods

Structure analysis and refinement was made using the SDP/PDP V.4.2 software package [9] operating on a PDP 11/73 computer. Perspective drawings were made with the ORTEP-III program [10]. Geometry analysis was performed using PARST. [11] Comparison with other structures was assisted by the use of the Cambridge Structural Database System (CSDS) and the associated software [12].

RESULTS AND DISCUSSION

Preparation

The complexes $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{Hdapsox})(\text{H}_2\text{O})](\text{ClO}_4)$ were obtained in a template synthesis starting from $\text{Cu}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ or

$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 2,6-diacetylpyridine (DAP) and semioxamazine (SOX) in a molar ratio 1:1:2. All attempts to influence the reaction products by altering the molar ratio of the reactants (e.g., 1:1:1 or 1:2:2) were unsuccessful. The reaction products were always mononuclear complexes with either a doubly or singly deprotonated form of the ligand. These were characterized by IR-spectroscopic and analytical methods and by conductance at room temperature. What is noteworthy is that complexes with fully protonated form, H_2dapsox , were not produced even under fairly strong acidic conditions.

Description of the structure

Selected structural parameters of $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ are listed in Tables 2 and 3. The $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ complex represents a monomeric structure (Fig. 1). This is most remarkable considering the fact that this type of ligand, with so many potential donor atoms, is very prone to the formation of polynuclear structures in coordination to Cu^{II} [5–7].

The dapsox^{2-} coordinates as a quadridentate ligand to the four equatorial sites of the copper(II) atom: through N(4) of the pyridine ring, hydrazine nitrogens N(2) and N(5) of both side arms of dapsox^{2-} , and O(1) of one of the terminal amide-carbonyl groups. Therefore it forms three fused metal-chelate rings: a central six-membered ring with five-membered rings at each side of it. The apical water, O(W1), completes the square pyramidal coordination environment of copper(II). The charge on the metal atom is neutralized by deprotonated nitrogen atoms N(2) and N(6).

Copper(II) is shown to be displaced from the equa-

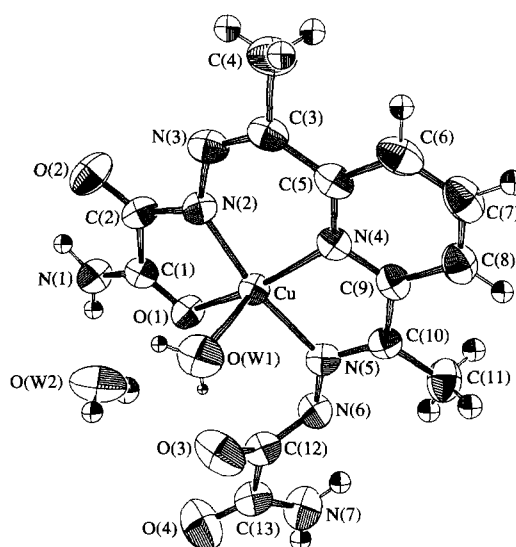


Fig. 1. ORTEP [10] view of the molecular structure of $[\text{Cu}(\text{dapsox})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ showing the thermal ellipsoids at the 50% probability level and the atom numbering scheme used in the tables.

Table 2. Fractional atomic coordinates for the non-hydrogen atoms of [Cu(dapsox)(H₂O)]·H₂O and equivalent isotropic thermal parameters, with e.s.d.s in parentheses

Cu	0.24763(5)	0.18390(4)	0.23685(4)	1.802(6)
O(W1)	0.5513(3)	0.3138(3)	0.3474(2)	2.83(5)
O(1)	0.1539(3)	0.3461(2)	0.3006(2)	2.21(4)
O(W2)	0.0660(4)	0.6356(3)	0.5007(3)	2.83(5)
O(2)	0.1263(3)	0.3943(2)	-0.0056(2)	3.09(5)
O(3)	0.4811(3)	0.3849(3)	0.5760(2)	3.53(6)
O(4)	0.3853(4)	0.5193(3)	0.7858(3)	4.49(7)
N(1)	0.0612(4)	0.5104(3)	0.2276(3)	2.41(6)
N(2)	0.1840(3)	0.2153(3)	0.0664(2)	1.97(5)
N(3)	0.1927(4)	0.1430(3)	-0.0592(2)	2.29(5)
N(4)	0.2591(3)	-0.0034(2)	0.1358(2)	1.82(5)
N(5)	0.2731(3)	0.1188(3)	0.3905(2)	1.96(5)
N(6)	0.2592(4)	0.1845(3)	0.5169(2)	2.33(5)
N(7)	0.2548(4)	0.3109(3)	0.7692(3)	3.23(6)
C(1)	0.1216(4)	0.4009(3)	0.2130(3)	1.95(6)
C(2)	0.1459(4)	0.3372(3)	0.0766(3)	2.04(6)
C(3)	0.2291(4)	0.0249(3)	-0.0834(3)	2.21(6)
C(4)	0.2267(5)	-0.0430(4)	-0.2284(3)	3.25(8)
C(5)	0.2666(4)	-0.0525(3)	0.0092(3)	1.92(6)
C(6)	0.3025(5)	-0.1815(4)	-0.0386(3)	2.64(7)
C(7)	0.3277(5)	-0.2564(3)	0.0432(4)	2.82(8)
C(8)	0.3122(5)	-0.2069(3)	0.1711(3)	2.48(7)
C(9)	0.2772(4)	-0.0786(3)	0.2147(3)	1.97(6)
C(10)	0.2664(4)	-0.0121(3)	0.3516(3)	2.02(6)
C(11)	0.2512(5)	-0.0923(3)	0.4371(3)	3.24(8)
C(12)	0.3622(4)	0.3161(3)	0.5919(3)	2.15(6)
C(13)	0.3337(4)	0.3923(3)	0.7264(3)	2.49(7)

torial (basal) plane O(1)—N(2)—N(4)—N(5) by 0.23 Å towards the apical water. The Cu—O(W1) bond is significantly longer than in most aqua complexes of Cu^{II} (average value [13] is 2.186 Å). However, this is not uncommon among the complexes of acyl hydrazides of DAP [14] (e.g. 2.394 Å in a dicopper(II) complex [15] of a hydroxylated bis(acetylsemicarbazone)-pyridine, and 2.137 and 2.346 Å in two dicopper(II) complexes with tetramine Schiff-base macrocycles derived from DAP) [16,17]. Other metal–ligand bond lengths are comparable to those found in other similar complexes [14]. Cu—N(2) and Cu—N(4) bonds of the six-membered metal–chelate ring are shorter than average (e.g., mean value [13] for Cu^{II}—N (Schiff base) is 1.96, and for Cu^{II}—N(py) it is 2.07 Å) while the bonds to outer ligands, O(1) and N(5), are slightly longer but still within the range found in DAP complexes [14]. This, together with the corresponding valence angles on Cu^{II} (see Table 2), indicates that the metal atom fits well into the six-membered ring with the bite angle almost approaching the ideal value of $\pi/2$, and that the ring strain is mostly localized on the bite angles of the five-membered rings as a result of obvious geometrical constraints.

The entire ring system is notably planar with only Cu and N(5) atoms displaced out of the calculated mean plane, in the same direction, by 0.33 and 0.32 Å,

respectively. The conformation of the six-membered metal–chelate ring can be viewed as a flattened half-boat (envelope) caused by a displacement of the Cu^{II} atom from the calculated mean plane of the ring by 0.26 Å. The total puckering amplitude [18] for this ring, Q , is 0.158. In comparison with the other known structures of the Schiff base derivatives of DAP [14], the present structure is unique in the sense that it has an unsymmetrical ring system containing one six-membered metal–chelate ring, and yet it is mononuclear. Rare examples [14] of copper complexes containing such structural fragment are aforementioned {[Cu₂(dip)Cl₂]H₂O}₂ [5], and the dicopper(II) complex [15] of the hydroxylated bis(acetylsemicarbazone)-pyridine, in which M(NNCCN) rings are formed in conjunction with fused five-membered M(NNCO) rings with another Cu^{II} atom, in tetranuclear and dinuclear structures, respectively. In both cases the six-membered rings have very flattened unsymmetrical boat conformations ($Q = 0.20$ and 0.18, respectively).

The pyridine ring is practically planar with bond distances and angles within the range for DAP complexes [14]. Both five-membered metal–chelate rings are only slightly puckered, which is evident from the torsional angles. The one involving the coordinated terminal carbonyl group tends towards an unsym-

Table 3. Bond distances (Å) and valence angles (°) for [Cu(dapsox)(H₂O)] · H₂O with e.s.d.s in parentheses

Cu—N(2)	1.909(3)	N(1)—C(1)	1.306(4)
Cu—N(4)	1.957(2)	N(2)—C(2)	1.349(4)
Cu—N(5)	1.986(3)	N(2)—N(3)	1.368(4)
Cu—O(1)	1.993(2)	N(3)—C(3)	1.290(5)
Cu—O(W1)	2.300(2)	N(4)—C(5)	1.339(4)
		N(4)—C(9)	1.348(5)
C(1)—C(2)	1.521(5)	N(5)—C(10)	1.296(5)
C(3)—C(4)	1.502(5)	N(5)—N(6)	1.383(4)
C(3)—C(5)	1.486(5)	N(6)—C(12)	1.320(4)
C(5)—C(6)	1.404(5)	N(7)—C(13)	1.317(6)
C(6)—C(7)	1.369(6)		
C(7)—C(8)	1.385(6)	O(1)—C(1)	1.252(4)
C(8)—C(9)	1.389(5)	O(2)—C(2)	1.225(5)
C(9)—C(10)	1.472(5)	O(3)—C(12)	1.238(5)
C(10)—C(11)	1.491(6)	O(4)—C(13)	1.214(4)
C(12)—C(13)	1.546(5)		
N(1)—C(1)—C(2)	115.6(4)	N(2)—Cu—N(4)	90.8(1)
O(1)—C(1)—C(2)	120.2(3)	N(4)—Cu—N(5)	82.8(1)
O(1)—C(1)—N(1)	124.2(3)	N(2)—Cu—N(5)	169.1(1)
N(2)—C(2)—C(1)	108.9(3)	N(2)—Cu—O(1)	83.5(2)
O(2)—C(2)—C(1)	121.1(4)	N(5)—Cu—O(1)	99.9(2)
O(2)—C(2)—N(2)	130.0(4)	N(4)—Cu—O(1)	162.4(1)
N(3)—C(3)—C(4)	113.7(4)	N(5)—Cu—O(W1)	94.2(1)
C(5)—C(3)—C(4)	117.1(3)	O(1)—Cu—O(W1)	95.4(1)
N(3)—C(3)—C(5)	129.2(3)	N(2)—Cu—O(W1)	95.8(2)
C(6)—C(5)—C(3)	120.0(3)	N(4)—Cu—O(W1)	101.8(1)
N(4)—C(5)—C(3)	120.7(3)		
N(4)—C(5)—C(6)	119.3(3)	C(1)—O(1)—Cu	110.3(3)
C(7)—C(6)—C(5)	120.1(3)	C(2)—N(2)—Cu	115.3(2)
C(6)—C(7)—C(8)	119.9(3)	N(3)—N(2)—Cu	130.4(2)
C(7)—C(8)—C(9)	118.1(4)	C(2)—N(2)—N(3)	113.7(3)
N(4)—C(9)—C(10)	115.4(4)	C(3)—N(3)—N(2)	120.6(4)
C(8)—C(9)—C(10)	123.1(3)	C(5)—N(4)—C(9)	121.1(3)
N(4)—C(9)—C(8)	121.4(3)	C(9)—N(4)—Cu	112.3(2)
C(9)—C(10)—C(11)	121.1(3)	C(5)—N(4)—Cu	126.3(2)
N(5)—C(10)—C(11)	123.9(3)	C(10)—N(5)—Cu	113.3(3)
N(5)—C(10)—C(9)	115.0(3)	N(6)—N(5)—Cu	128.3(2)
N(6)—C(12)—C(13)	112.9(3)	C(10)—N(5)—N(6)	116.9(3)
O(3)—C(12)—C(13)	115.9(2)	C(12)—N(6)—N(5)	113.3(3)
O(3)—C(12)—N(6)	131.1(3)		
N(7)—C(13)—C(12)	115.7(3)		
O(4)—C(13)—C(12)	119.6(4)		
O(4)—C(13)—N(7)	124.6(4)		

metrical envelope conformation (puckering parameter $q = 0.14$) and the other, involving one of the hydrazine nitrogens of the pendant arm, tends towards a skew conformation ($q = 0.09$).

All intraligand bond distances are well within the normal range [14]. However, noteworthy is the inequality between the semicarbazone arms. The bond lengths of the N—C—C—O fragment forming the five-membered metal-chelate ring are significantly different from those of the pendant fragment. The C(1)—O(1) double bond lengthens upon coordination of O(1), as expected, but this change is accompanied by the lengthening of the C(2)—N(2) and shortening of the C(1)—C(2) ring bonds in comparison to the corresponding bonds of the pendant

fragment. It is plausible that the coordination causes a slight delocalization involving the exo carbonyl group C(2)—O(2) and the ring bond C(1)—C(2), but such a difference does not seem to be discernible in the values of bond angles around trigonal carbon atoms since they merely demonstrate the exact coplanarity of substituents on all C atoms. The relative lengthening of the C(2)—N(2) ring bond is followed by a slight shortening of the N(2)—N(3) bond of the adjacent hydrazine fragment of the six-membered ring, in comparison to the bond lengths of the pendant semicarbazone arm. However, both N—N bonds are distinctly shorter than normal single bonds and longer than normal double bonds, which is a clear indication of the π electron delocalization due to double depro-

Table 4. Hydrogen bond distances (Å) and angles (°) for [Cu(dapsox)(H₂O)]·H₂O

Hydrogen bond	Donor symmetry	D—H	H···A	D···A	D—H···A
N(1)—H1N1···W(2)		0.956	1.894	2.826	164.07
N(1)—H2N1···O(2)	-x, 1-y, -z	0.952	2.050	2.943	155.37
N(7)—H2N7···O(2)	x, y, z-1	0.950	2.053	2.949	156.48
W(1)—H1W1···O(3)		0.765	1.912	2.666	168.33
W(1)—H2W1···O(4)	1-x, 1-y, 1-z	0.769	2.039	2.761	156.42
W(2)—H1W2···W(1)	1-x, 1-y, 1-z	0.784	2.062	2.825	164.56
W(2)—H2W2···O(1)	-x, 1-y, 1-z	0.764	2.685	3.277	135.84

tonation of dapsox²⁻. In a related Cr^{III} complex with singly deprotonated 2,6-diacetylpyridinebis(semicarbazone) Bino *et al.* [21] have found an increase in the N—N length rather than a decrease and attributed it to the relief of the ring strain in the five-membered M(NNCO) chelate ring. In our structure, both N—N bonds are significantly shortened, as expected. Following Bino's argument, [21] this might be an explanation for the preferred formation of a six-membered rather than five-membered metal-chelate ring. Furthermore, if one semicarbazone arm forms a six-membered ring, then the other cannot fully engage its ligand atoms and must remain pendant for steric reasons.

Crystal packing of [Cu(dapsox)(H₂O)]·H₂O is dictated by van der Waals interactions and some strong inter- and intramolecular hydrogen bonds (Table 4). A particularly prominent intramolecular hydrogen bond exists between the H₂O ligand and the O(3) of the hydrazide carbonyl group of the pendant arm. Atom O(4) of the amide-carbonyl group and N(7) of the terminal amino group of the pendant arm form intermolecular hydrogen bonds to H₂O ligand and O(2) from the exo carbonyl group of the five-membered metal-chelate ring, respectively. These hydrogen bonds probably fix the conformation of the pendant semicarbazone arm. The H₂O molecule of crystallization is anchored by one strong hydrogen bond to the amide nitrogen N(1) as a donor, and two moderate hydrogen bonds to the H₂O ligand and O(1) of the five-membered metal-chelate ring. Finally, the amino group N(1) forms an intermolecular hydrogen bond to O(2) acceptor of the exo carbonyl group. All the intermolecular hydrogen bonds are largely responsible for the centrosymmetric packing of the complex molecules in the crystal lattice.

Infrared spectra

Infrared spectra were assigned for [Cu(dapsox)(H₂O)]·H₂O on the basis of the known crystal structure, and for [Cu(Hdapsox)(H₂O)](ClO₄) by comparison. A more detailed description of the IR spectra is given in our previous papers [3,4] dealing with Co^{II} complexes of H₂dapsox. Therefore we shall confine our discussion to the comparison of the IR

spectra for Cu^{II} complexes with singly and doubly deprotonated forms of H₂dapsox. The noticeable similarity of these spectra suggests the same coordination behaviour of dapsox²⁻ and Hdapsox⁻. If that is the case, then it is a reasonable assumption that N(6) of the pendant arm is protonated in the [Cu(Hdapsox)(H₂O)](ClO₄) structure. A single strong band observed at 3118 cm⁻¹ in the spectrum of [Cu(Hdapsox)(H₂O)](ClO₄) is therefore ascribed to the stretching vibration of the secondary NH group of the pendant arm. For the same reason additional stretching C=O vibrations in the 1630–1730 cm⁻¹ region appear in the spectrum of [Cu(Hdapsox)(H₂O)](ClO₄) of which the strong band at 1716 cm⁻¹ is also present in the spectrum of fully protonated free ligand, H₂dapsox, and in its Co(II) complex [4]. Finally, an amide-II band at 1512 cm⁻¹ appears in the spectrum of [Cu(Hdapsox)(H₂O)](ClO₄) which is absent from the spectrum of doubly deprotonated [Cu(dapsox)(H₂O)]·H₂O. The presence of ClO₄⁻ counterion is clearly demonstrated by the ν₄ band of medium intensity at 626 cm⁻¹ and the very strong band at ca 1100 cm⁻¹ (ν₃) characteristic for ionic perchlorates [22].

Acknowledgements—The authors would like to express their gratitude to Drs Michael Burnett and Carroll Johnson, as well as to Professor Mario Nardelli for making their programs available through Internet. The work was supported by the Serbian Research Council (Contracts No. 02E09 and 02E35).

REFERENCES

- Pelizzi, C., Pelizzi, G., Predieri, G. and Vitali, F., *J. Chem. Soc., Dalton Trans.*, 1985, 2387.
- Sommerer, S. O., Baker, J. D., Zerner, M. C. and Palenik, G. J., *Inorg. Chem.*, 1992, **31**, 563.
- Andjelković, K., Ivanović, I., Prelesnik, B. V., Leovac, V. M. and Poleti, D., *Polyhedron*, 1996, **15**, 4361.
- Ivanović, I., Andjelković, K., Beljanski, V., Prelesnik, B. V., Leovac, V. M. and Momirović, M., *J. Coord. Chem.*, in press.
- Mangia, A., Pelizzi, C. and Pelizzi, G., *Acta Cryst.*, 1974, **B30**, 2146.

6. Lorenzini, C., Pelizzi, C., Pelizzi, G. and Predieri, G., *J. Chem. Soc., Dalton Trans.*, 1983, 2155.
7. Lorenzini, C., Pelizzi, C., Pelizzi, G. and Predieri, G., *J. Chem. Soc., Dalton Trans.*, 1983, 721.
8. Pelizzi, C., Pelizzi, G. and Vitali, F., *J. Chem. Soc., Dalton Trans.*, 1987, 177.
9. Frenz, B. A., E-N: *Structure Determination Package*, Version 4.2. Enraf-Nonius, Delft, The Netherlands (1982).
10. Burnett, M. N. and Johnson, C. K., ORTEP-III: Oak Ridge Thermal Ellipsoid Plotting Program For Crystal Structure Illustrations, ORNL-6895, Oak Ridge Natl Lab., Oak Ridge, Tennessee, July 1996.
11. Nardelli, M., *J. Appl. Crystallogr.*, 1995, **28**, 659.
12. Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., MacCrae, C. F., Mitchell, E. M., Smith, J. M. and Watson, D. G., *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187; Allen, F. H., Kennard, O. and Taylor, R., *Acc. Chem. Res.*, 1983, **16**, 146.
13. Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. and Taylor, R., *J. Chem. Soc., Dalton Trans. (Suppl.)*, 1989, p. S1.
14. A search of the CSDS (V4.30) revealed 120 crystal structures of metal complexes with various Schiff base derivatives of DAP. Comparisons of the ring conformations were done using specific examples from this collection. Comparisons of bond distances were done using the average values from the selected subsets of the collection.
15. Koziol, A. E., Palenik, R. C. and Palenik, G. J., *J. Chem. Soc., Chem. Commun.*, 1989, 650.
16. McKee, V., Smith, J., *J. Chem. Soc., Chem. Commun.*, 1983, 1465.
17. Bailey, N. A., Fenton, D. E., Moody, R., Rodriguez de Barbarin, C. O., Sciambarella, I. N., Latour, J.-M., Limosin, D. and McKee, V., *J. Chem. Soc., Dalton Trans.*, 1987, 2519.
18. Cremer, D. and Pople, J. A., *J. Am. Chem. Soc.*, 1975, **97**, 1354.
19. Brewer, G. A., Sinn, E., *Inorg. Chem.*, 1984, **23**, 2532.
20. Palenik, G. J. and Giordano, T. J., *J. Chem. Soc., Dalton Trans.*, 1987, 1175.
21. Bino, A., Frim, R. and van Genderen, M., *Inorg. Chim. Acta*, 1987, **127**, 95.
22. Brown, L. C., Begun, G. M. and Boyd, G. E., *J. Am. Chem. Soc.*, 1969, **91**, 2250; Hathaway, B. J. and Underhill, A. E., *J. Chem. Soc.*, 1961, 3091.