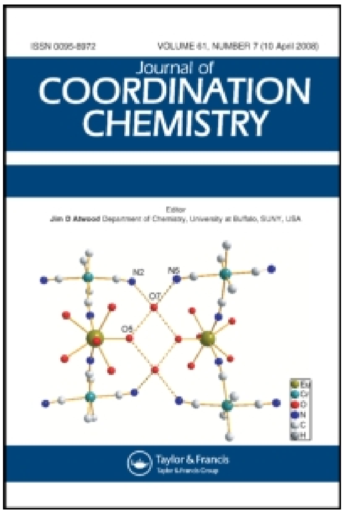

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization and magnetochemical studies of some imidazole and imidazolate copper(II) complexes derived from *N*-salicylideneacetylhydrazine: X-ray crystal and molecular structures of [imidazole-(*N*-salicylidenatoacetylhydrazinato)-ONO' (-2)]copper(II) and potassium [mono(μ-imidazolate) bis(*N*-salicylidenatoacetylhydrazinato)] dicopper(II)

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To cite this Article Iskander, Magdi F. , Khalil, Tarek E. , Haase, Wolfgang , Foro, Sabine and Lindner, Hans J.(2005) 'Synthesis, characterization and magnetochemical studies of some imidazole and imidazolate copper(II) complexes derived from *N*-salicylideneacetylhydrazine: X-ray crystal and molecular structures of [imidazole-(*N*-salicylidenatoacetylhydrazinato)-ONO' (-2)]copper(II) and potassium [mono(μ-imidazolate) bis(*N*-salicylidenatoacetylhydrazinato)] dicopper(II)', Journal of Coordination Chemistry, 58: 2, 111 — 123

To link to this Article: DOI: 10.1080/00958970410001710080

URL: http://dx.doi.org/10.1080/00958970410001710080

Journal of Coordination Chemistry
Vol. 58, No. 2, 20 January 2005, 111–123

Synthesis, characterization and magnetochemical studies of some imidazole and imidazolate copper(II) complexes derived from *N*-salicylideneacetylhydrazine: X-ray crystal and molecular structures of [imidazole-(*N*-salicylidenatoacetylhydrazinato)-ONO′ (-2)]copper(II) and potassium [mono(μ-imidazolate) bis(*N*-salicylidenatoacetylhydrazinato)] dicopper(II)

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(Received 11 July 2003; revised 12 October 2003; in final form 4 January 2004)

Three new copper(II) complexes, [Cu(Sah)HIm], [Cu(HSah)Cl · HIm] and K[{Cu(Sah)}$_2$Im], have been prepared and characterized by elemental analyses, infrared and ultraviolet–visible spectroscopy (HSah and Sah refer to mono- and dinegative *N*-salicylideneacetylhydrazine anions, respectively, while HIm and Im refer to neutral imidazole and mononegative imidazolate anion). The X-ray crystal and molecular structures of [Cu(Sah)HIm] and K[{Cu(Sah)}$_2$Im] have been determined. In [Cu(Sah)HIm], the copper(II) atom is in a distorted square-planar environment and coordinated to the hydrazone ligand via phenoxy oxygen, imine nitrogen and deprotonated enolimine oxygen. The fourth coordination site is occupied by the imidazole nitrogen. The imidazole N–H is involved in an intermolecular hydrogen bond with the hydrazide nitrogen forming a 1-D supramolecular structure. In the (μ-imidazolate) dicopper(II) complex K[{Cu(Sah)}$_2$Im], each copper(II) atom is in a distorted square-planar environment where the hydrazone ligand acts as an ONO tridentate dianion. The imidazolate anion acts as a bridged coligand connecting the two tricoordinated copper(II) units. The K$^+$ is six coordinate, coordinated to four (μ-imidazolate) dicopper(II) units giving rise to a supramolecular network. Both [Cu(Sah)HIm] and [Cu(HSah)Cl · HIm] show normal magnetic moments of 1.82 and 1.85 μ_β respectively. The dicopper complex K[{Cu(sah)}$_2$Im] shows antiferromagnetic spin–spin coupling mediated via the μ-imidazolate with $-J = 17.0\,\mathrm{cm}^{-1}$.

Keywords: *N*-Salicylideneacetylhydrazine copper(II) complexes; Imidazole; Imidazolate complexes; X-ray molecular structures; Infrared spectra; Ultraviolet–visible spectra; Magnetic properties

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001710080

1. Introduction

The reaction of N-salicylideneacylhydrazines (H_2L) with copper(II) salts gave either mononuclear, $[Cu(HL)X \cdot H_2O]$ ($X = Cl$ or NO_3), or dinuclear $[\{Cu(L)\}_2]$ copper(II) complexes [1–10] depending on the experimental conditions. These complexes show a wide spectrum of biological activities, but their mode of action is still unclear [11–14]. The observed biological activities may be related to their ability to interact with different biological heterocyclic bases such as the imidazolyl residue in histidine or other similar residues. Recently, the reaction of mononuclear, $[Cu(HL)Cl \cdot H_2O]$ (figure 1, structure **1**, $R = C_6H_5$, p-$CH_3C_5H_4$, p-$CH_3OC_6H_4$ and p-ClC_6H_4) and dinuclear $[\{Cu(L)\}_2]$ (figure 1, structure **2**, $R = C_6H_5$, p-$CH_3C_5H_4$, p-$CH_3OC_6H_4$ and p-ClC_6H_4) copper(II) complexes derived from N-salicylidenearoylhydrazines with imidazole were studied and a number of imidazole and μ-imidazolate complexes were prepared and characterized [15]. X-ray structure analyses reveal that the structure of the imidazole copper(II) complex depends on the nature of R in the aroylhydrazone ligand. With an electron-withdrawing substituent ($R = p$-ClC_6H_5), the isolated imidazole complex $[Cu(Sp\text{-}ClBzh)HIm] \cdot H_2O$ is monomeric with copper(II) coordinated to the dinegative ONO tridentate aroylhydrazone, the fourth coordination

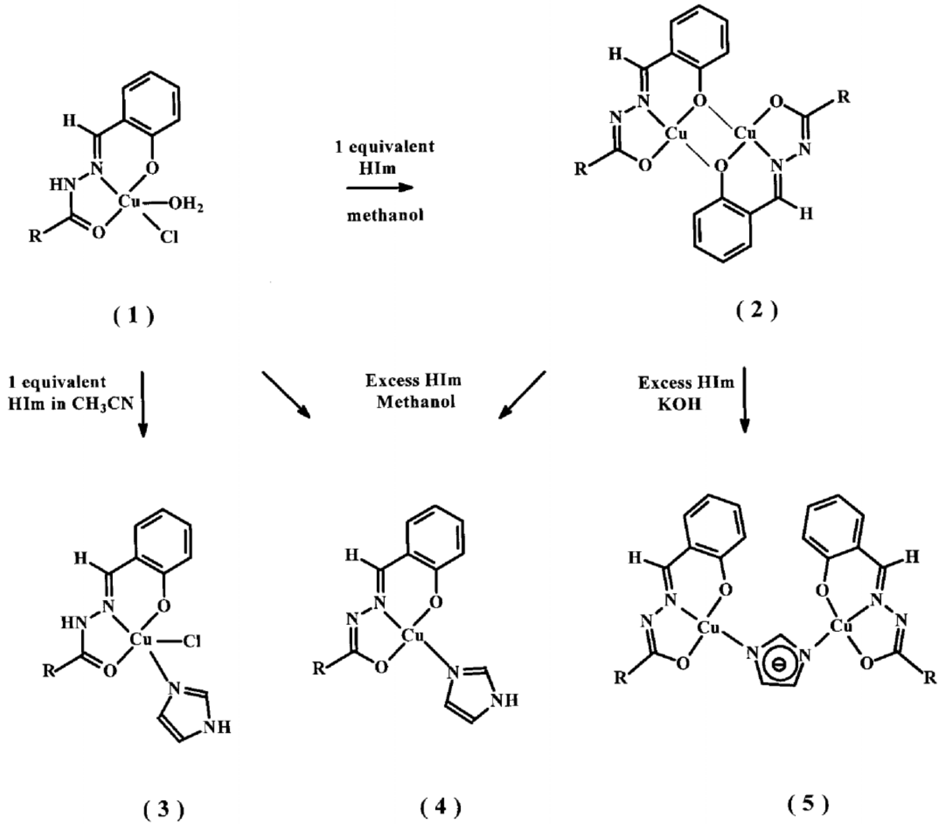

Figure 1. Schematic representation of the reaction of imidazole with $[Cu(HL)Cl \cdot H_2O]$ and $[\{Cu(L)\}_2]$ complexes.

site being occupied by imidazole nitrogen [15]. However, in the presence of an electron-releasing substituent (R $= p$-$CH_3C_6H_5$), dimerization via phenoxy oxygens is favored and the dimeric complex [{Cu(Sp-CH_3Bzh)HIm}$_2$]·H_2O was isolated. A series of anionic mono (μ-imidazolate) copper(II) complexes, K[CuL–Im–CuL], were also prepared and their magnetic properties were discussed, but no X-ray structural data for any of these complexes have been reported [15].

In this article we wish to describe the synthesis and X-ray structures of both imidazole and (μ-imidazolate) copper(II) complexes derived from *N*-salicylideneacetylhydrazine (H_2Sah). The magnetic properties of the isolated complexes are also discussed.

2. Experimental

2.1 *Materials*

Imidazole (Aldrich) was used without further purification. *N*-Salicylideneacetylhydrazine (H_2Sah) was prepared by the condensation of salicylaldehyde with acetylhydrazine in methanol (m.p. = 199–200°C, Lit, 198–199°C) [16]. The corresponding monomeric chloro copper(II) complex [Cu(HSah)Cl·H_2O], figure 1, Structure **1** (R = Me), and dimeric neutral complex [{Cu(Sah)}$_2$], figure 2, Structure **2** (R = Me), were prepared as previously described [3].

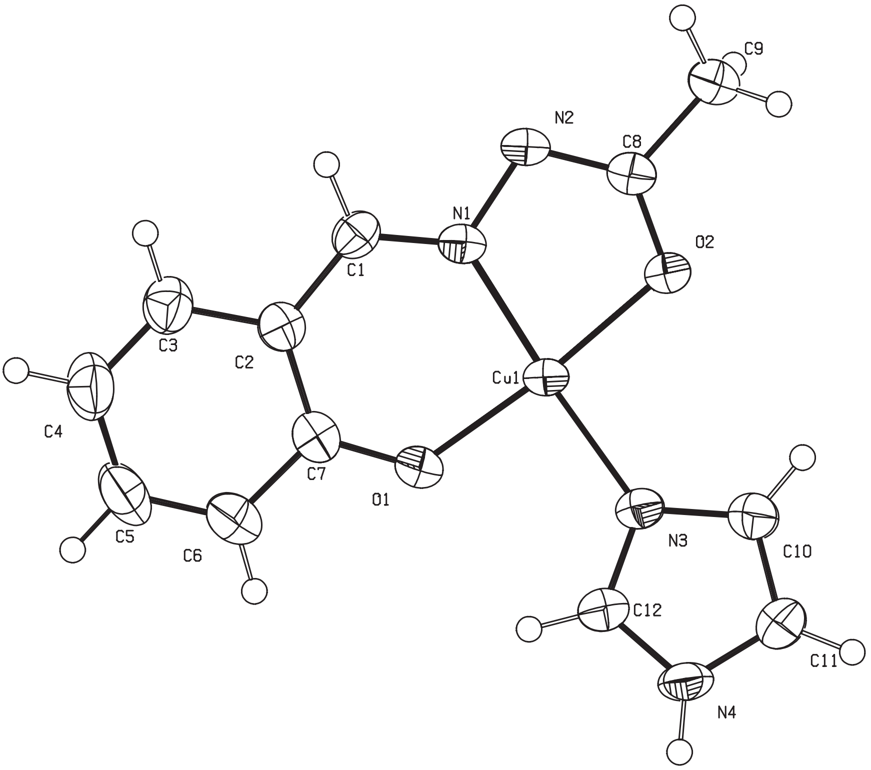

Figure 2. X-ray structure of [Cu(Sah)HIm] 50% probability ellipsoids.

2.2 *Preparation of [Cu(Sah)HIm]*

To a hot suspension of [{Cu(Sah)}$_2$] (1.0 mmol) in methanol (30 cm^3) an excess of imidazole (5.0–6.0 mmol) was added. The reaction mixture was heated under reflux until complete dissolution of the [{Cu(sah)}$_2$] complex then boiled under reflux, with constant stirring, for a further 15 min. On cooling, crystals of [Cu(sah)HIm], figure 1, Structure **4** (R = Me), suitable for X-ray diffraction measurements precipitated. The isolated complex was filtered, washed with diethylether and then dried in vacuum. Yield: 72%. Anal. Calcd. for $C_{12}H_{12}N_4O_2Cu$ (%): C, 46.83; H, 3.93; N, 18.20; Cu, 20.65. Found: C, 46.95; H, 3.96; N, 18.41; Cu, 20.61. Ft-IR relevant frequencies (cm^{-1}): 3145 ν(N–H), 3048, 2937, 2857 ν(C–H), 2807, 2708, 2652, 2615 [ν(N–H) + ν(C–H)], 1615 ν(C=N–N=C). UV–Vis (solvent, λ_{max}/nm (log ε): MeCN, 258 (4.10), 298 (4.05), 313 (3.99), 370 (3.98), 570 (2.35); MeOH, 256 (4.15), 284 (4.06), 295 (4.07), 309 (4.03), 371 (3.94), 598 (2.03). Magnetic moment: μ_{eff} (298 K) = 1.82 μ_β.

2.3 *Preparation of [Cu(HSah)Cl·HIm]*

A solution of imidazole (2.0 mmol) in acetonitrile (10 cm^3) was added to a suspension of [Cu(HL)Cl · H_2O] (figure 1, Structure **1** R = Me) (1.0 mmol) in acetonitrile (40 cm^3). The reaction mixture was boiled under reflux with constant stirring for 30 min. The reaction mixture was left to cool and the formed complex [Cu(HSah)Cl · HIm] (figure 1, Structure **3**, R = Me) was filtered, washed with diethylether then dried in vacuum. Yield: 78%. Anal. Calcd. for $C_{12}H_{13}N_4O_2CuCl$ (%): C, 41.87; H, 3.81; N, 16.27; Cu, 18.46; Cl, 10.30. Found: C, 41.81; H, 3.84; N, 16.32; Cu, 18.48; Cl, 10.28.

Ft-IR relevant frequencies (cm^{-1}): 3200, [hydrazone ν(N–H)]; 3150 [imidazole ν(N–H)]; 3062, 3014, 3048, 2937, 2857 ν(C–H); 2807, 2708, 2652, 2615 [ν(N–H) + ν(C–H)]; 1620 [amide I band, ν(C=O)]; 1600 [ν(C=N) + ν(C=C)]; 1525 [amide II band, δ(N–H)]. Magnetic moment: μ_{eff} (298 k) = 1.85 μ_β.

2.4 *Preparation of K[(Sah)Cu·Im·Cu(Sah)]*

To a suspension of the neutral dimer [{Cu(Sah)}$_2$] (figure 1, Structure **2**, R = Me) (1.0 mmol) in dry methanol (50 cm^3), excess KOH (5.0 mmol) was added. The reaction mixture was refluxed for about one hour, until complete dissolution, and then filtered. To the clear filtrate, imidazole (0.01 mol) was added and the reaction mixture was further boiled under reflux for *ca.* 1 h, and then evaporated to dryness. The isolated crude product was recrystallized from acetonitrile–benzene (1 : 1) mixture and dried in a vacuum. Yield: 58%. Anal. Calcd. for $C_{21}H_{19}N_6O_4Cu_2K$ (%): C, 43.07; H, 3.44; N, 14.35; Cu, 21.70. Found: C, 43.15; H, 3.40; N, 14.39; Cu, 21.60. Ft-IR relevant frequencies (cm^{-1}): 3085, 3062, 3014, 2927, ν(C–H); 1618 ν(C=N–N=C); 1599 ν(C=C). UV–Vis (solvent, λ_{max}/nm (log ε): MeCN, 258 (4.24), 299 (4.20), 313 (4.13), 377 (4.11), 579 (2.38), MeOH, 256 (4.59), 283 (4.49), 295 (4.50), 310 (4.46), 370 (4.37), 600 (2.46). Magnetic moment: μ_{eff} (298 K) = 1.78 μ_β.

2.5 *Physical measurements*

Elemental (carbon, hydrogen and nitrogen) analyses were carried out at the Microanalytical Laboratory, Institute für Organische Chemie, Technische

Universität, Darmstadt, Germany. Infrared spectra were recorded on a Perkin-Elmer 1430 Data system and/or a Perkin-Elmer PARAGON 1000 PC infrared spectrophotometer. Spectrophotometric measurements in the visible and ultraviolet regions were made by a UV–Vis double beam ratio recording, Perkin-Elmer model LAMBADA 4B. Magnetic susceptibilities of powdered dried samples were recorded on a Faraday-type magnetometer using a sensitive computer-controlled D-200 Cahn RG microbalance in the temperature range 4.2–298 K. The magnetic field applied was ~1.5 T. Details of the apparatus have been described elsewhere [17]. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants [18].

2.6 *X-ray crystal and molecular structure*

X-ray diffraction measurements were carried out on an Oxford diffraction Xcalibur™ single-crystal X-ray diffractometer with Sapphire CCD detector. The structures of [Cu(Sah)HIm] and K[(Sah)CuImCu(Sah)] were solved by the direct method using the SHELXS-97 [19] and refined by full-matrix least-squares methods on all F^2 data using the SHELXL-97 [20] programs.

3. Results and discussion

3.1 *Synthesis*

The reaction of dimeric [{Cu(Sah)}$_2$] (figure 1, Structure **2**, R = Me) with excess imidazole (HIm) afforded the corresponding imidazole complex [Cu(Sah)HIm] (figure 1, structure **4**, R = Me). On the other hand, the reaction of [Cu(HSah)Cl(H$_2$O)] · H$_2$O (figure 1, Structure **1**, R = Me) with one equivalent of imidazole in methanol proceeded with deprotonation of the hydrazide proton and eventually gave the dimer, [{Cu(Sah)}$_2$], while the reaction of [Cu(HSah)Cl(H$_2$O)] · H$_2$O with a large excess of imidazole gave [Cu(HSah)HIm], identical to that obtained from the reaction of [{Cu(Sah)}$_2$] with imidazole. In acetonitrile as solvent, the reaction of the chloro complex with imidazole gave the corresponding chloro imidazole [Cu(HSah)Cl · HIm] (figure 1, Structure **3**, R = Me) with no sign of deprotonation. In the presence of KOH, however, the reaction of imidazole with [{Cu(sah)}$_2$] in methanol afforded the corresponding (μ-imidazolate) complex K[(Sah)Cu–Im–Cu(Sah)] (figure 1, Structure **5**, R = Me).

3.2 *Infrared and UV–Vis spectra*

The IR spectrum of the monoimidazole adduct [Cu(Sah)HIm] lacks absorption from aroylhydrazone ν(N–H), amide I [ν(C=O)], amide II [δ(N–H)], but shows the imidazole ν(N–H) at *ca.* 3140 cm^{-1} with a series of bands within the range 3090–2600 cm^{-1} attributed to ν(C–H) and coupled vibrations [ν(N–H) + ν(C–H)] of imidazole. The spectrum of [Cu(HSah)Cl · HIm] shows both the acetylhydrazone and the imidazole ν(N–H) at 3200 and 3144 cm^{-1}, respectively. The spectrum also displays bands due to coordinated amide I [ν(C=O), ν(C=N)], amide II and amide III bands implying that the acylhydrazone is coordinated to the central copper(II) via deprotonated phenoxy oxygen, azomethine nitrogen and deprotonated enolimine oxygen. In these adducts, the acylhydrazone is a dianionic ONO tridentate ligand while the fourth coordination site of the central copper(II) is occupied by the imidazole nitrogen. The IR spectrum of the μ-imidazolate dicopper(II) complex lacks absorptions due to ν(N–H), amide I [ν(C=O)], and amide II [δ(N–H)] of the acetylhydrazone ligand as well as ν(N–H) of the imidazole coligand, suggesting that each copper(II) is coordinated to the dinegative ONO tridentate acetylhydrazone while the imidazolate ion acts as a bridging coligand.

The electronic spectra of [Cu(Sah)HIm] and K[(Sah)Cu–Im–Cu(Sah)] in acetonitrile are similar and show a series of bands at 258, 298, 313 and 370 nm due to different intraligand transitions. The LMCT band [from deprotonated enolimine oxygen to copper(II)] which is expected to appear at 370–380 nm is probably hidden under the intense intraligand charge transfer at 370 nm. The spectra show an absorption at 570 nm characteristic of the Cu(II) d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition ($^2B_{1g} \rightarrow {}^2E_g$) in a square-planar ligand field. In methanol the d–d band suffers a red shift and appears at 597 nm [21].

3.3 *X-ray Structures of [Cu(Sah)HIm] and K[(Sah)Cu–Im–Cu(Sah)]*

The crystal data and structure refinement parameters for both [Cu(Sah)HIm] and K[(Sah)Cu–Im–Cu(Sah)] are given in table 1. Some selected bond lengths (Å) and angles (°) recorded for [Cu(Sah)HIm] and K[(Sah)Cu–Im–Cu(Sah)] are listed in tables 2 and 3, respectively.

The copper(II) in [Cu(Sah)HIm], figure 2, is in a distorted square planar environment and is coordinated to the acetylhydrazonate ligand *via* the deprotonated

Table 1. Crystal data and structure refinement for [Cu(Sah)HIm] and K[{Cu(Sah)}$_2$Im].

Complex	[Cu(Sah)HIm]	K[{Cu(Sah)}$_2$ Im]
Empirical formula	$C_{12}H_{12}CuN_4O_2$	$C_{21}H_{19}Cu_2KN_6O_4$
Formula weight	307.8	585.6
Temperature (K)	299(2)	299(2)
Wavelength (Å)	0.71093	0.71093
Crystal system, space group	Orthorombic, *P*bca	Monoclinic, *C*2/*c*
Unit cell dimensions (Å,°)	$a = 6.476(1)$	$a = 9.835(1)$
	$b = 21.657(3)$	$b = 21.719(2)$ $\beta = 102.723(8)$
	$c = 18.818(3)$ $\gamma = 90$	$c = 10.869(1)$
Volume (Å^3)	2639.2(7)	2264.7(4)
Z, Calculated density (Mg m^{-3})	8, 1.549	4, 1.718
Absorption coefficient (mm^{-1})	1.658	2.104
F(000)	1256	1184
Crystal size (mm)	0.375 × 0.15 × 0.075	0.45 × 0.25 × 0.125
θ range for data collection (°)	1.88–25.99	1.88–25.97
Limiting indices	$-7 \le h \le 1$, $-26 \le k \le 25$, $0 \le l \le 23$	$-12 \le h \le 2$, $-26 \le k \le 0$, $-13 \le l \le 13$
Reflections collected/unique	4644/2579 [*R*(int) = 0.0425]	2848/2216 [*R*(int) = 0.0176]
Completeness to $\theta = 25.99$ (%)	99.90	100.0
Absorption correction	Empirical from ψ-scan	Empirical from ψ-scan
Max. and min. transmission	0.8616 and 0.7041	0.7314 and 0.5445
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2579/0/172	2216/0/184
Goodness-of-fit on F^2	1.002	1.052
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0308$, $wR2 = 0.0836$	$R1 = 0.0227$, $wR2 = 0.0635$
R indices (all data)	$R1 = 0.0609$, $wR2 = 0.0949$	$R1 = 0.0327$, $wR2 = 0.0671$
Largest diff. peak and hole (e Å^{-3})	0.634 and −0.384	0.232 and −0.447

Table 2. Selected bond lengths (Å) and angles (°) for [Cu(Sah)HIm].

Copper(II) polyhedron			
Cu(1)–O(1)	1.8924(18)	O(1)–Cu(1)–N(3)	90.53(8)
Cu(1)–N(3)	1.960(2)	O(2)–Cu(1)–N(3)	94.89(8)
Cu(1)–O(2)	1.9426(18)	O(2)–Cu(1)–N(1)	81.40(8)
Cu(1)–N(1)	1.914(2)	N(1)–Cu(1)–O(1)	93.45(9)
		O(1)–Cu(1)–O(2)	174.24(8)
		N(2)–Cu(1)–N(1)	172.11(9)
		C(10)–N(2)–Cu(1)	129.41(19)
		C(12)–N(3)–Cu(1)	124.75(18)
Hydrazone ligand			
O(1)–C(7)	1.306(3)	O(1)–C(7)–C(2)	124.40(2)
C(7)–C(2)	1.419(4)	C(7)–C(2)–C(1)	123.20(2)
C(2)–C(1)	1.433(4)	C(2)–C(1)–N(1)	123.90(2)
C(1)–N(1)	1.291(3)	N(1)–N(2)–C(8)	109.10(2)
N(1)–N(2)	1.404(3)	N(2)–C(8)–O(2)	124.10(2)
N(2)–C(8)	1.324(4)		
C(8)–O(2)	1.281(3)		
C(8)–C(9)	1.492(4)		
Imidazole ring			
N(3)–C(12)	1.306(4)	N(3)–C(12)–N(4)	111.60(2)
C(12)–N(4)	1.328(3)	C(12)–N(4)–C(11)	107.30(2)
N(4)–C(11)	1.353(4)	N(4)–C(11)–C(10)	106.90(4)
C(11)–C(10)	1.348(4)	C(11)–C(10)–N(3)	108.40(3)
C(10)–N(3)	1.377(3)	C(10)–N(3)–C(12)	105.8(2)
Hydrogen bonds			
N(2)···HN(4)#	2.0229	N(2)···H–N(4)#	173.12

Operators for generating equivalent atoms # x, $-y+1/2$, $z+1/2$.

phenoxy oxygen O(1), azomethine nitrogen N(1) and deprotonated enolimide oxygen O(2). The Cu(1)–O(1) [1.8924(18) Å], Cu(1)–N(1) [1.914(2) Å], and Cu(1)–O(2) [1.9426(18) Å] bond distances are shorter than those reported for [Cu(HSah)Cl(H_2O)]·H_2O where Cu(1)–O(1) = 1.907(2), Cu(1)–N(1) = 1.940(2) and Cu(1)–O(1) = 1.992(2) Å [4]. This can be attributed to the reduction of Cu(II) coordination number as well as the delocalization of the negative charge created on N(2) as a result of the deprotonation of the hydrazide moiety in [Cu(Sah)HIm]. The fourth coordination site in [Cu(Sah)HIm] is occupied by the imidazole nitrogen N(3). The Cu(1)–N(3) bond distance (1.960 Å) lies within the lower end of the range previously reported for Cu–N(HIm) distances of imidazole copper(II) complexes [22–28]. The distortion from regular square planar is seen in the departure from 180° of the angles O(1)–Cu(1)–O(2) [174.24(8)], N(1)–Cu(1)–N(3) [172.11(9)], and from 90° of the bite angles N(1)–Cu(1)–O(1) [93.45(9)], N(1)–Cu(1)–O(2) [81.40(8)°]. A similar coordination mode was reported for [Cu(Sp-ClBzh)HIm]·H_2O [15], where Sp-ClBzh^{2-} refers to the *N*-salicylidene-*p*-chlorobenzoylhydrazine dianion. The N–H imidazole proton is involved in an intermolecular hydrogen bond with the hydrazo nitrogen N(2) forming a 1-D supramolecular structure as shown in figure 3. The hydrogen bond distances and angles are shown in table 2.

The structure of the potassium [mono(μ-imidazolate)-bis-(*N*-salicylidenatoacetylhydrazinato)] dicopper(II) complex K[(Sah)Cu–Im–Cu(Sah)], figure 4, consists of a dicopper(II) anion [Cu(Sah)$_2$Im]$^-$ where each copper(II) atom Cu(1) is in a distorted square-planar environment and is coordinated to the ONO tridentate acetylhydrazone

Table 3. Selected bond lengths (Å) and angles (°) for $\mathrm{K[\{Cu(Sah)\}_2Im]}$.

Copper(II) polyhedron			
Cu(1)–O(1)	1.9088(14)	O(1)–Cu(1)–N(1)	91.73(6)
Cu(1)–N(2)	1.9076(16)	N(1)–Cu(1)–O(2)	95.80(6)
Cu(1)–O(2)	1.9357(13)	O(2)–Cu(1)–N(2)	81.66(6)
Cu(1)–N(1)	1.9467(16)	N(2)–Cu(1)–O(1)	93.69(6)
		O(1)–Cu(1)–O(2)	166.52(6)
		N(1)–Cu(1)–N(2)	165.64(7)
Hydrazone ligand			
C(3)–O(1)	1.3210(3)	O(1)–C(3)–C(8)	123.96(18)
C(3)–C(8)	1.4420(3)	C(3)–C(8)–C(9)	123.45(18)
C(8)–C(9)	1.4370(3)	C(8)–C(9)–N(2)	124.00(18)
C(9)–N(2)	1.2860(3)	C(9)–N(2)–Cu(1)	126.10(14)
N(2)–N(3)	1.4030(2)	N(3)–N(2)–Cu(1)	114.79(13)
C(10)–N(3)	1.3190(3)	N(2)–N(3)–C(10)	108.43(15)
C(10)–O(2)	1.2830(3)	N(3)–C(10)–O(2)	124.95(18)
C(10)–C(11)	1.4910(3)	C(10)–O(2)–Cu(1)	110.10(13)
		N(3)–C(10)–C(11)	117.80(2)
μ-imidazolate			
C(2)–N(1)	1.332(2)	C(1)–N(1)–C(2)	104.75(17)
C(1)–N(1)	1.379(3)	N(1)–C(1)–C(1) #1	108.54(11)
C(1)–C(1) #1	1.351(4)	N(1)–C(2)–N(1) #1	113.40(2)
Potassium polyhedron			
K(1)–N(1)	3.0039(17)	O(1)–K(1)–O(1) #3	180.0
K(1)–O(1)	2.8668(14)	O(1)–K(1)–N(3) #2	73.86(5)
K(1)–N(3) #2	2.8681(17)	O(1) #3–K(1)–N(3) #2	106.14(5)
K(1)–N(1) #3	3.0039(17)	O(1)–K(1)–N(3) #4	106.14(5)
K(1)–O(1) #3	2.8668(14)	O(1) #3–K(1)–N(3) #4	73.86(5)
K(1)–N(3) #4	2.8681(17)	N(3) #2–K(1)–N(3) #4	180.0
		O(1)–K(1)–N(1) #3	123.81(4)
		O(1) #3–K(1)–N(1) #3	56.19(4)
		N(3) #2–K(1)–N(1) #3	91.85(5)
		N(3) #4–K(1)–N(1) #3	88.15(5)
		O(1)–K(1)–N(1)	56.19(4)
		O(1) #3–K(1)–N(1)	123.81(4)
		N(3) #2–K(1)–N(1)	88.15(5)
		N(3) #4–K(1)–N(1)	91.85(5)
		N(1) #3–K(1)–N(1)	180.0

Symmetry transformations used to generate equivalent atoms: #1: $-x, y, -z+1/2$; #2: $-x+1, y, -z+1/2$; #3: $-x+1/2, -y+1/2, -z+1$; #4: $x-1/2, -y+1/2, z+1/2$.

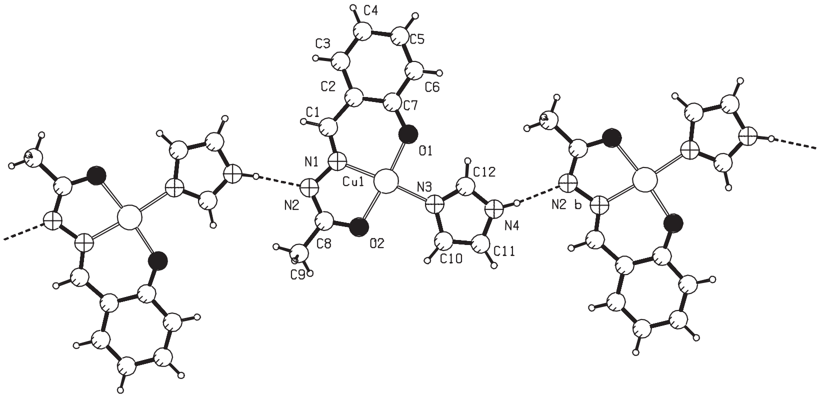

Figure 3. Hydrogen bonds in [Cu(Sah)HIm].

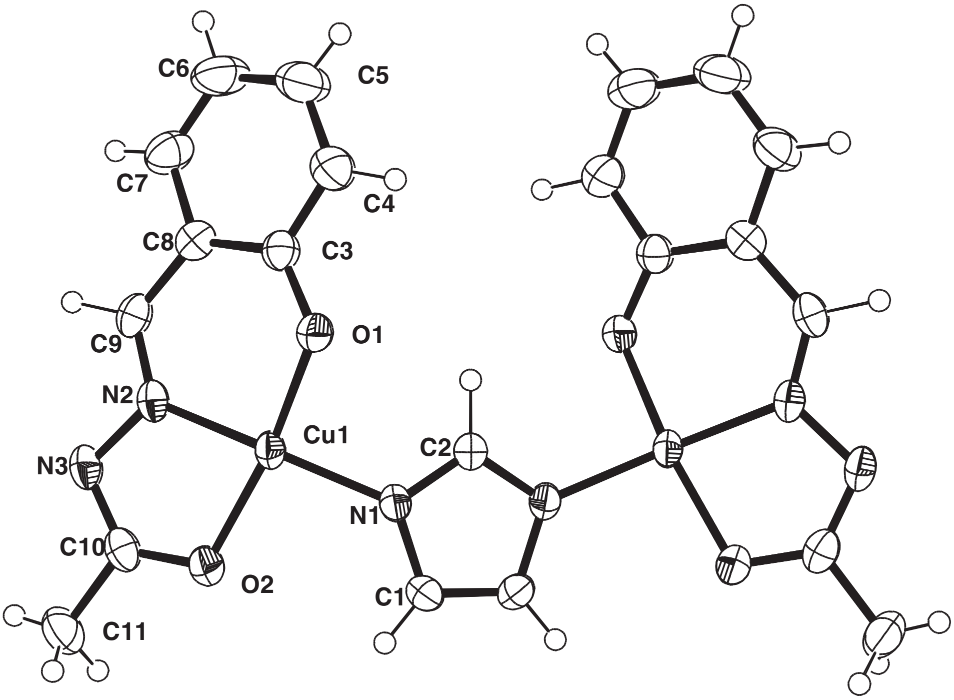

Figure 4. X-ray structure of $[(\mathrm{Sah})\mathrm{Cu}\text{-}\mathrm{Im}\text{-}\mathrm{Cu}(\mathrm{Sah})]^{1-}$ 50% probability ellipsoids.

dianion. The fourth coordination site is occupied by the imidazolate nitrogen N(1). The imidazolate anion acts as a bridge connecting the two identical [*N*-salicylidenatoacetylhydrazinato copper(II)] units. The imidazolate ring is nearly planar, with 0.01 Å the largest deviation from the mean plane. As in many imidazolate-bridged copper(II) complexes, the imidazolate N(1)–C(2)–N(1)#1 angle [113.4(2)] is larger while C(1)–N(1)–C(2) [104.75(17)] are smaller than 108° [29]. The Cu(1)–N(1) bond distance, [1.9467(16)], falls within the range (1.92–2.00 Å) reported for other Cu–N(Im) bond distances [29–31]. Cu(1) is displaced by 0.012 Å from the Cu(1), N(1), O(1), N(2), O(2) plane. The dihedral angle between the imidazolate ring and the copper(II) coordination plane (ϕ angle) is 25.3°. The Cu(1)–N(1)–C(2) (α angle) (122.5°) is comparable to those reported for other (μ-imidazolate) dicopper(II) complexes [29–31].

Each K cation is in an octahedral environment. The coordination polyhedron around the potassium atom, figure 5, is completed by [O(1), N(1)]′ and [O(1), N(1)]″ of two different (μ-imidazolate) dicopper units in addition to [N(3)‴, N(3)⁗] of two additional, different (μ-imidazolate) dicopper units. Thus each (μ-imidazolate) dicopper(II) unit is coordinated to four different potassium cations. The first potassium cation (K′) is attached to the [N(1), O(1)]′ atoms while the other [N(1), O(1)]′ set of the same molecule is attached to the second potassium cation (K″). The third and fourth potassium cations (K‴, K⁗) attach, respectively, to two hydrazone nitrogens [N(3), N(3)′] of the same dicopper unit. The coordination of the potassium cation with four different (μ-imidazolate) dicopper(II) units gives rise to a supramolecular network.

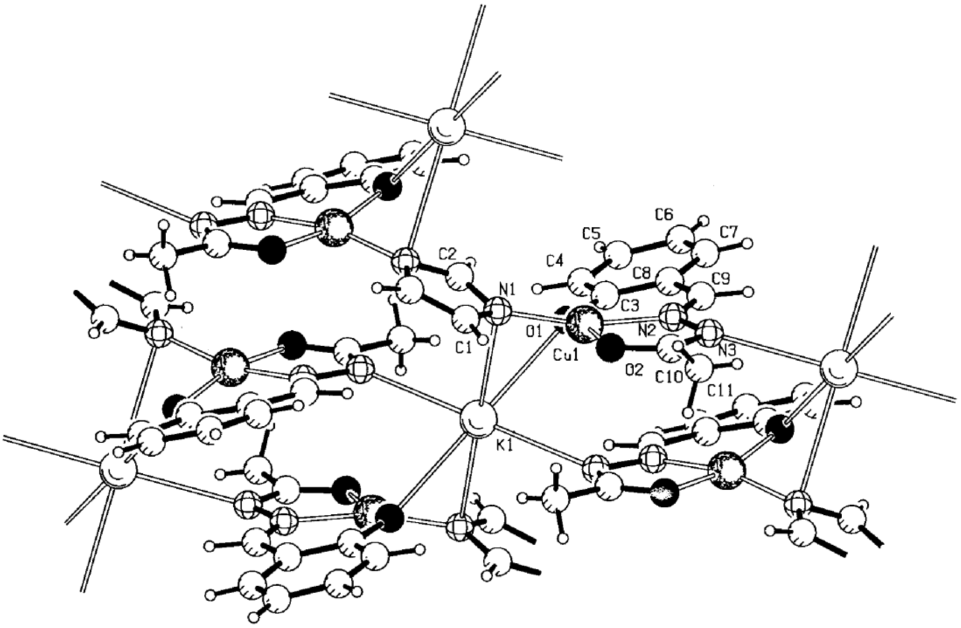

Figure 5. K$^+$ ion polyhedron.

3.4 *Magnetic measurements*

The room temperature magnetic moments of [Cu(Sah)HIm] ($\mu_{\mathrm{eff}} = 1.82\,\mu_\beta$) and [Cu(HSah)Cl · HIm] ($\mu_{\mathrm{eff}} = 1.85\,\mu_\beta$), are within the range reported for magnetically dilute mononuclear copper(II) complexes [21], in agreement with the X-ray molecular structure of [Cu(Sah)HIm] given in figure 2, where no Cu–Cu interactions are expected.

The room temperature magnetic moment per copper recorded for the mono (μ-imidazolate) dinuclear copper(II) complex [(Sah)Cu–Im–Cu(Sah)] ($1.78\,\mu_\beta$) is slightly higher than the spin-only value ($1.73\,\mu_\beta$) calculated for paramagnetic copper(II) complexes. However, variable-temperature magnetic susceptibility measurements in the temperature range 4.2–298 K, suggest an antiferromagnetic exchange interaction between the two copper(II) centers mediated by the imidazolate ion. A plot of χ_{M} versus T, figure 6, shows a maximum around 30 K. This behavior is typical of antiferromagnetic-coupled dinuclear imidazolate-bridged copper(II) complexes [15,30, 34–36]. The variable-temperature magnetic susceptibility data were fitted to the revised Bleaney–Bowers equation [37], using the isotropic exchange Hamiltonian ($H = -2S_1S_2$) for two interacting $S = 1/2$ centers,

$$\chi_{\mathrm{M}} = (1-\rho)\frac{2N_{\mathrm{L}}\mu_\beta^2 g^2 \exp(2J/kT)}{\mathrm{k}(T-\theta)(1+3\exp(2J/kT))} + \rho\frac{2N_{\mathrm{L}}\mu_\beta^2 g^2}{4kT} + 2N_\alpha \qquad (1)$$

where N_α is the temperature-independent paramagnetism, ρ is the mole fraction of monomeric impurity and θ is a correction term for interdimer interaction. Other terms have their usual meaning. The obtained $2J$ (cm^{-1}), g, and ρ values are -34.0, 2.17, and 0.005, respectively.

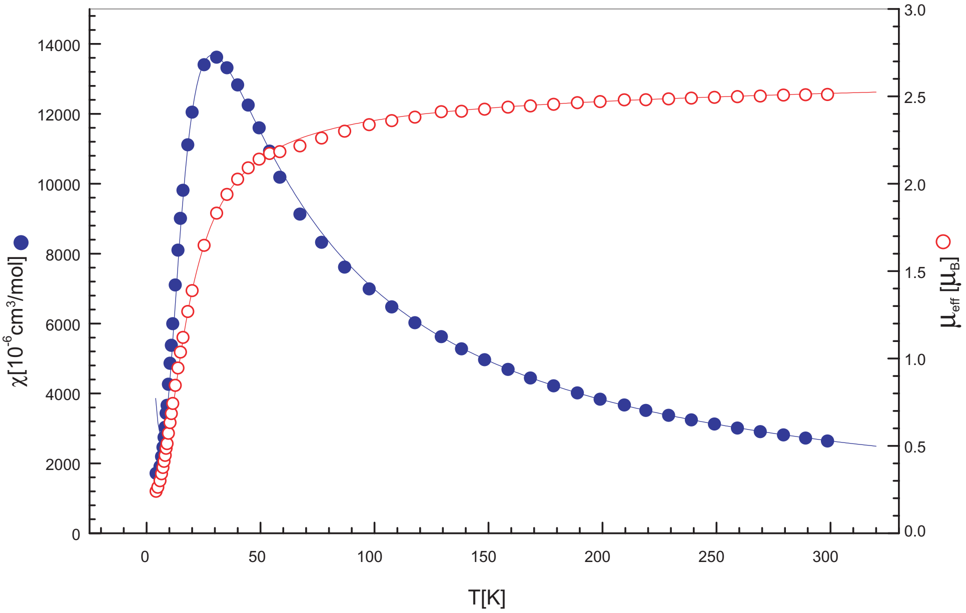

Figure 6. Magnetic susceptibilities χ(●) and magnetic moments (○) vs. temperature for K[(Sah)Cu-Im-Cu(Sah)]. Solid lines represent the best least squares fit to Bleany-Bavers equation with $J = -17.0$, $g = 2.07$ and $p = 0.005$.

Magnetochemical studies on μ-imidazolate-bridged dinuclear copper(II) complexes [29–36,38–40] show that the magnitude of antiferromagnetic exchange coupling ($-2J$) mediated by the imidazolate bridge depends mainly on the Cu–N(Im)–C(Im) (α) or Cu–N(Im)–N′(Im) (θ) angle which affect the degree of overlap between the σ-antibonding $d_{x^2-y^2}$ orbitals of the copper(II) and nitrogen lone pair orbitals of the imidazolate ion. An increase in either α or θ would improve the orbital overlap and increase the $-2J$ value, reaching a maximum when Cu–N(Im) vectors are parallel to the imidazolate C–C bond, $\alpha = 144°$ [30,36] . The dihedral angle (φ) between the copper(II) coordination plane and the imidazolate plane also affects, but to a lesser extent, the observed $-2J$ value. Also an increase in φ results in a decrease in $-2J$ value.

In exogenic imidazolate dicopper(II) complexes, the angle α is generally in the range 120–135° and $2J$ values vary from -34 to $-76\,\text{cm}^{-1}$ [29–36,38–40]. The ($-2J$) value recorded in the present work for [(sah)Cu–Im–Cu(sah)]$^-$ is within the lower limit of this range. This can be related to the relatively small α angles ($\alpha_1 = \alpha_2 = 122°$). More or less similar $-2J$ values have been recently reported for a series of related anionic μ-imidazolate dicopper(II) complexes derived from *N*-salicylidenearoylhydrazines [15], implying similar coordination spheres and nearly identical Cu–Im–Cu dimensions. The $-2J$ ($34\,\text{cm}^{-1}$) as well as the angles α (122°) and φ (25.3°) recorded for [(sah) Cu–Im–Cu(sah)]$^-$ can be compared with those of [Cu$_2$(gly-glyO)$_2$(Im)]$^-$ ($\alpha_1 = 124.5°$, $\alpha_2 = 124.1°$, $\varphi_1 = 5.8°$, $\varphi_2 = 10.4°$ and $-2J = 38.2\,\text{cm}^{-1}$) [29] which is the only anionic exogenic imidazolate bridged complex characterized by X-ray structure analysis. The smaller $-2J$ value of [(sah)Cu–Im–Cu(sah)]$^-$ relative to that of [Cu$_2$(gly-glyO)$_2$(Im)]$^-$ can be attributed to the smaller α angle and larger ϕ dihedral angle.

Supplementary data

Atomic coordinates, equivalent isotropic displacement parameters, hydrogen coordinates, isotropic displacement parameters, anisotropic displacement parameters and complete lists of bond distances and bond angles of [Cu(sah)HIm] and $K[\{Cu(sah)\}_2Im]$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 216123 and CCDC 216124, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgments

Thanks are due to BMBF/Forschungszentrm, Jüelich, and ÖA-IB/Wo WTZ for supporting this bilateral project.

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