

Study of bis(iminodiacetato)cuprates(II) and tetrakis(iminodiacetato)cuprates(II)

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Received 17 December 1982

Compounds of the type $M_2[Cu(ida)_2] \cdot nH_2O$ and $M'_4H_2[Cu(ida)_4] \cdot mH_2O$, where $M = Li^+, Na^+, K^+$; $M' = H^+, Li^+, Na^+, K^+, 1/2Ba^{2+}$ and $ida = HN(CH_2COO^-)_2$, were prepared. The infrared and electronic spectra, the EPR spectra, and the stability constants in aqueous solution were studied with the compounds prepared. The results obtained indicated the octahedral configuration of the donor atoms around copper and the preferential formation of complexes with the copper-to-ida mole ratio of 1:2 with the alkali metals and 1:4 with Ba^{2+} and H^+ .

Синтезированы соединения типа $M_2[Cu(ida)_2] \cdot nH_2O$ и $M'_4H_2[Cu(ida)_4] \cdot mH_2O$ где $M = Li^+, Na^+, K^+$; $M' = H^+, Li^+, Na^+, K^+, 1/2Ba^{2+}$ и $ida = HN(CH_2COO^-)_2$. Изучены ИК-, электронные и ЭПР-спектры, а также константы устойчивости в водном растворе полученных соединений. Полученные результаты свидетельствуют об октаэдрическом размещении донорных атомов вокруг атома меди и о предпочтительном образовании комплексов с мольным отношением медь:ida равным 1:2 при щелочных металлах и 1:4 при Ba^{2+} или H^+

Iminodiacetic acid forms metal complexes with metal-to-ida ratios ($\alpha_i = x(i\text{-metal}) : x(ida)$) of $\alpha_i = 1:1$ or $1:2$. For complexes with the lanthanides, $\alpha_i = 1:3$ has also been reported [1]. Complexes of copper with iminodiacetic acid with $\alpha_i = 1:2$ have been primarily studied in solution [2—7]. The stability constant values obtained indicate that the bis(iminodiacetato)cuprate(II) anion is most stable in the series of the studied divalent cations from the first row of the transition metals [7]. Among the complexes of iminodiacetic acid with copper, the following have been studied in the solid state: $Cu(ida) \cdot 2H_2O$ and $K_2[Cu(ida)_2] \cdot H_2O$, the structures of which have been determined by X-ray analysis [8—10], and $Na_2[Cu(ida)_2] \cdot 10H_2O$, the electronic and IR spectra and the thermal decomposition of which have been studied [11]. For $Na_2[Cu(ida)_2] \cdot 10H_2O$, the conditions for the preparation and for optimal crystallization have also been studied [12, 13]. It

follows from the above papers that $\text{Cu}(\text{ida}) \cdot 2\text{H}_2\text{O}$ has a polymeric character with bidentate coordination of the carboxyl group. The bis(iminodiacetato)cuprate(II) complexes are monomeric, with monodentate coordination of both carboxyl groups and the coordination of the nitrogen atoms in the *trans*-facial position. The present paper is aimed at the preparation of copper complexes with iminodiacetic acid with $\alpha_{\text{Cu}} > 1:2$ and at a study of the properties of the compounds prepared.

Experimental

The magnetic susceptibility was measured at 298 K by the Faraday method using a balance calibrated with copper(II) sulfate pentahydrate and sodium chloride.

The IR spectra were obtained on a UR-20 instrument (Zeiss, Jena) within the region of $\tilde{\nu} = 400\text{--}4000\text{ cm}^{-1}$ in KBr pellets, from 400 cm^{-1} to 1800 cm^{-1} in a nujol mull and from 1800 cm^{-1} to 3800 cm^{-1} in tripene.

The diffuse reflectance spectra of the solids were measured on a VSU-2 instrument (Zeiss, Jena) using magnesium oxide as a reference material, in the region of $\tilde{\nu}$ from 200 nm to 1100 nm.

The absorption electronic spectra of aqueous solutions were obtained on a Varian Cary 17 spectrophotometer in the region of $\tilde{\nu}$ from 400 nm to 1300 nm and at a concentration 0.2 mol dm^{-3} .

The EPR spectra were measured on a Varian E-4 x-band spectrometer, using aqueous solutions of the complexes with a concentration of $10^{-2}\text{ mol dm}^{-3}$ or microcrystalline magnetically undiluted powders.

Potentiometric titrations were carried out in an argon atmosphere presaturated with the solvent vapours at $(25 \pm 0.1)^\circ\text{C}$ and $I(\text{NaClO}_4) = 0.1\text{ mol dm}^{-3}$, using a GK 2301 combined electrode and a PHM 64 pH-meter (Radiometer, Copenhagen). The instrument was calibrated to yield $-\log[\text{H}^+]$, directly with a precision of 0.005 units, by titration of mixtures of perchloric and acetic acid with a standard carbonate-free sodium hydroxide solution. The best values of γ_{H^+} , K_w , and E_j were calculated from the dissociation constant of acetic acid, assuming complete dissociation of perchloric acid and sodium hydroxide, using a least-squares program for the $-\log[\text{H}^+]$, range of 2 to 12.

During the data processing, a tentative calculation [14] of the complex formation curves, \bar{n} vs. $-\log[\text{L}]$, proved that no polynuclear complex was formed in the system and that the equilibria were attained instantaneously, as the two titration types were always consistent. The protonation constants for the ligand, required in the calculation, were taken from a previous paper [15]. In the $\text{Cu}/\text{H}_2\text{ida}$ system, a significant dependence of the \bar{n} vs. $-\log[\text{L}]$ curve on the initial solution acidity was observed, indicating the presence of protonated complexes.

The complex compositions and corresponding estimates of the stability constants, found from the formation curves, were used as the input parameters for the statistical MINQUAD program [16]. The optimum parameters were sought by systematically varying the set of the input complex compositions, any new complex being considered acceptable if the overall error of the function decreased at least by 20 %; this decrease roughly corresponds to twice

that caused by the total cumulation of the experimental errors, as confirmed by a tentative processing of biased input values of the solution composition, consumption, and $-\log [H^+]$, for a typical data set.

In the prepared substances, the alkali metals were determined by atomic absorption spectrometry, copper chelatometrically after sample combustion and dissolution of the residue in hydrochloric acid and nitrogen by distillation as NH_3 after the sample mineralization. Water was determined from the weight loss on stationary drying from 50 °C to 200 °C and from the difference of the analyses up to 100 mass %. The iminodiacetic acid preparation was obtained from SAS Scientific Chemicals and the other chemicals were the products of Lachema, Brno.

Preparations

The $Cu(ida) \cdot 2H_2O$, $Li_2[Cu(ida)_2] \cdot H_2O$, $Na_2[Cu(ida)_2] \cdot 8H_2O$, and $K_2[Cu(ida)_2] \cdot H_2O$ complexes were prepared from basic copper(II) carbonate, iminodiacetic acid, and the appropriate hydroxide by the methods described in the literature [8—10]. The analogous barium salt could not be prepared even when varying the ratio of the reactants, pH, and temperature. The resultant compound was always $Ba_2H_2[Cu(ida)_4] \cdot 12H_2O$ alone or in a mixture with $Cu(ida) \cdot 2H_2O$. The complexes ($\alpha_i = 1:4$) were successfully prepared in the case of $H_6[Cu(ida)_4] \cdot 2H_2O$ and $Li_4H_2[Cu(ida)_4] \cdot 4H_2O$ by a change in the reactant ratio. $Na_4H_2[Cu(ida)_4] \cdot 10H_2O$ and $K_4H_2[Cu(ida)_4] \cdot 3H_2O$ could only be prepared by the conversion from the barium salt followed by precipitation with ethanol.

$H_6[Cu(ida)_4] \cdot 2H_2O$ was prepared by dissolving 4.6 g of iminodiacetic acid and 1.1 g of copper(II) carbonate hydroxide in 100 cm³ of water. The solution was evaporated to one half of the initial volume and the substance was precipitated with ethanol.

$Ba_2H_2[Cu(ida)_4] \cdot 12H_2O$ was prepared by dissolving 5 g of iminodiacetic acid and 1.1 g of copper(II) carbonate hydroxide in 100 cm³ of water, followed by the addition of 6.1 g of barium hydroxide, evaporating the solution to one half of the initial volume and allowing it to crystallize. The crystals separated were washed with ether and ethanol.

$Li_4H_2[Cu(ida)_4] \cdot 4H_2O$ was prepared by subsequent dissolution of 0.013 mol of copper(II) carbonate hydroxide and 0.052 mol of lithium hydroxide in a concentrated aqueous solution of 0.065 mol of iminodiacetic acid. The solution obtained was partially evaporated and allowed to crystallize. The crystals separated were washed with ethanol and ether.

$Na_4H_2[Cu(ida)_4] \cdot 10H_2O$ and $K_4H_2[Cu(ida)_4] \cdot 3H_2O$ were prepared by the conversion of $Ba_2H_2[Cu(ida)_4] \cdot 12H_2O$ with the appropriate sulfate in an approx. 10 mass % solution. The $BaSO_4$ formed was filtered off and the complex salt was precipitated with ethanol.

Results and discussion

Dehydration of copper(II) iminodiacetate, lithium, sodium, and potassium bis(iminodiacetato)cuprate(II), and tetrakis(iminodiacetato)cupric acid was completed below a temperature of 180 °C. Dehydration of the studied salts of tetrakis(iminodiacetato)cupric acid was completed at 150 °C, except for two water

Table 1
Analytical and physical data of the studied complexes

Substance	Results of analyses								IR spectrum		Molar susceptibility $\chi_M \cdot 10^{-3}$ $\text{dm}^3 \text{mol}^{-1}$
	$w(\text{M})/\%$		$w(\text{Cu})/\%$		$w(\text{N})/\%$		$w(\text{H}_2\text{O})/\%$		$\tilde{\nu}/\text{cm}^{-1}$	antisym. N—H —COO ⁻	
	found	calc.	found	calc.	found	calc.	found	calc.			
Cu(ida)·2H ₂ O	—	—	27.69	27.55	6.02	6.07	15.5*	15.6	1585	3180 3275	1.47
Li ₂ [Cu(ida) ₂]·H ₂ O	3.94	3.88	17.62	17.77	7.81	7.83	4.9*	5.0	1625	3210 3260	1.28
Na ₂ [Cu(ida) ₂]·8H ₂ O	9.02	8.92	12.33	12.32	5.59	5.43	27.6*	27.5	1620	3275 3300	1.24
K ₂ [Cu(ida) ₂]·H ₂ O	18.78	18.53	14.97	15.06	6.59	6.64	4.1*	4.3	1625	3240 3290	1.35
H ₆ [Cu(ida) ₂]·2H ₂ O	—	—	10.18	10.08	8.92	8.88	6.3** 5.5*	5.7	1585	3110 3260	1.12
Li ₄ H ₂ [Cu(ida) ₄]·4H ₂ O	3.95	4.02	9.14	9.21	8.13	8.12	10.8** 5.52*	10.5	1595	3060—3100 3190 sh 3210 vs	0.80
Na ₄ H ₂ [Cu(ida) ₄]·10H ₂ O	10.02	10.24	7.02	7.07	6.32	6.24	23.8** 20.8*	24.1	1580	3210 3210 1615 1630 sh	0.68
K ₄ H ₂ [Cu(ida) ₄]·3H ₂ O	19.29	19.54	7.90	7.94	7.12	7.00	6.2** 3.3*	6.75	1600	3020 3200 1640	0.48
Ba ₂ H ₂ [Cu(ida) ₄]·12H ₂ O	24.82	25.46	5.85		5.20	5.19	20.6** 17.8*	20.0	1580	3040 3180 3200	1.05

* Values found from thermal decomposition.

** Values found from the difference of analyses up to 100 %.

molecules that were dissociated only during the ligand decomposition at a temperature higher than 200 °C, which suggests their possible coordination. The measured values of magnetic susceptibility of the prepared complexes (Table 1) are in a good agreement with the published values [17].

In the study of the IR spectra, attention was centred on the stretching vibrations of the carboxyl group and of the N—H group, from the point of view of the coordination of the two groups to the central atom (Table 1). The absorption band of the antisymmetrical vibration of the carboxyl group is shifted to $\tilde{\nu} = 1625\text{--}1655\text{ cm}^{-1}$ with the bis(iminodiacetato)cuprate(II) complexes and with the tetrakis(iminodiacetato)cuprate(II) complexes the band is split and shifted to $\tilde{\nu} = 1580\text{--}1640\text{ cm}^{-1}$. In the spectrum of $\text{H}_6[\text{Cu}(\text{ida})_4] \cdot 2\text{H}_2\text{O}$, an intense band was found at $\tilde{\nu} = 1715\text{ cm}^{-1}$, corresponding to the antisymmetrical stretching vibration of the —COOH group. The absorption bands of the stretching vibration of the N—H group were shifted to lower values of $\tilde{\nu}$ by 40 cm^{-1} on average for the bis(iminodiacetato)cuprate(II) complexes and by 100 cm^{-1} for the tetrakis(iminodiacetato)cuprate(II) complexes, compared with the absorption band in the K_2ida spectrum. The shifts of the absorption bands of the antisymmetrical stretching vibration of the carboxyl group and of the stretching vibration of the N—H group for the $\text{M}_2[\text{Cu}(\text{ida})_2]$ complex type correspond to the determined coordination of the two groups [8—11]. The shifts of the absorption bands of the N—H stretching vibration in $\text{M}_4\text{H}_2[\text{Cu}(\text{ida})_4]$ indicate more stronger Cu—N bonding than in the $\text{M}_2[\text{Cu}(\text{ida})_2]$ complexes. The splitting and shift of the absorption band of the antisymmetrical stretching vibration of the carboxyl group to $\tilde{\nu} = 1580\text{ cm}^{-1}$ with $\text{M}_4\text{H}_2[\text{Cu}(\text{ida})_4]$ can be explained by the ionic character of the uncoordinated —COO[−] groups. Another possible explanation, bidentate coordination of the carboxyl group similar to that in $\text{Cu}(\text{ida}) \cdot 2\text{H}_2\text{O}$ [8], is improbable in view of the number of the carboxyl groups. In the spectra of the studied salts of tetrakis(iminodiacetato)cupric acid, absorption bands corresponding to the —COOH group were not found in the region of $\tilde{\nu} = 1700\text{--}1800\text{ cm}^{-1}$.

The electronic spectra of all the studied complexes in aqueous solutions, *i.e.* $\text{Cu}(\text{ida}) \cdot 2\text{H}_2\text{O}$, $\text{M}_2[\text{Cu}(\text{ida})_2]$, and $\text{M}_4\text{H}_2[\text{Cu}(\text{ida})_4]$, are virtually identical (Fig. 1).

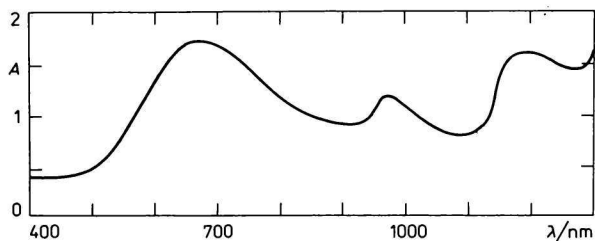


Fig. 1. Electronic absorption spectrum of the $\text{Cu}(\text{ida}) \cdot 2\text{H}_2\text{O}$, $[\text{Cu}(\text{ida})_2]^{2-}$, and $\text{H}_2[\text{Cu}(\text{ida})_4]^{4-}$ complexes in aqueous solutions.

A broad absorption band with a maximum at $\lambda = 650\text{--}700$ nm can be attributed to the ${}^2T_{2g} \leftarrow {}^2E_g$ transition, and bands at $\lambda = 970$ and 1190 nm may indicate tetragonal distortion [18]. The diffuse reflectance spectra of the solids are different, in dependence on the complex type. The shift of the absorption bands of the ${}^2T_{2g} \leftarrow {}^2E_g$ transition to the shorter wavelengths can be compared using the wavelengths given in Table 2, from $\lambda = 720\text{--}740$ nm ($\text{Cu}(\text{ida}) \cdot 2\text{H}_2\text{O}$) to $600\text{--}660$ nm ($[\text{Cu}(\text{ida})_2]^{2-}$) and $540\text{--}620$ nm ($[\text{Cu}(\text{ida})_4]^{6-}$). This shift corresponds to the increasing number of the coordinated nitrogen atoms [18].

Table 2
Diffuse reflectance spectra

Substance	Assignment					
	C.T./nm	$\lambda(T_{2g} \leftarrow E_g)/\text{nm}$				
$\text{Cu}(\text{ida}) \cdot 2\text{H}_2\text{O}$	275					720—740
$\text{Li}_2[\text{Cu}(\text{ida})_2] \cdot \text{H}_2\text{O}$	260		540 sh	600	630 sh	670 sh
$\text{Li}_4\text{H}_2[\text{Cu}(\text{ida})_4] \cdot 4\text{H}_2\text{O}$	270	500 sh	540	590		675 sh
$\text{Na}_2[\text{Cu}(\text{ida})_2] \cdot 8\text{H}_2\text{O}$	270				610 sh	660
$\text{Na}_4\text{H}_2[\text{Cu}(\text{ida})_4] \cdot 10\text{H}_2\text{O}$	260		560 sh		620	700 sh
$\text{K}_2[\text{Cu}(\text{ida})_2] \cdot \text{H}_2\text{O}$	260			605	625 sh	660
$\text{K}_4\text{H}_2[\text{Cu}(\text{ida})_4] \cdot 3\text{H}_2\text{O}$	265			600	625 sh	680 sh
$\text{H}_6[\text{Cu}(\text{ida})_4] \cdot 2\text{H}_2\text{O}$	260		550 sh			680
$\text{Ba}_2\text{H}_2[\text{Cu}(\text{ida})_4] \cdot 12\text{H}_2\text{O}$	260, 280		540		635	

All the studied complexes yield a broad intense EPR signal at values of the magnetic field lower than that corresponding to DPPM that was used as an internal standard (Fig. 2). The signals exhibit a strong anisotropy, but hyperfine structure

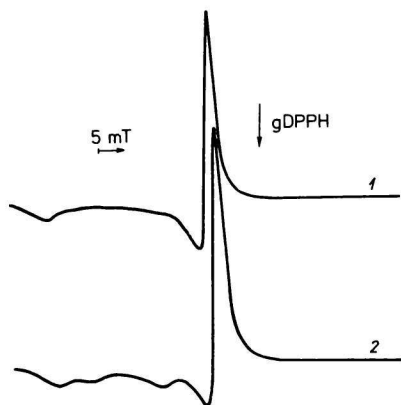


Fig. 2. EPR spectra of $\text{Na}_2[\text{Cu}(\text{ida})_2] \cdot 8\text{H}_2\text{O}$ (curve 1) and $\text{Na}_4\text{H}_2[\text{Cu}(\text{ida})_4] \cdot 10\text{H}_2\text{O}$ (curve 2) in the solid state.

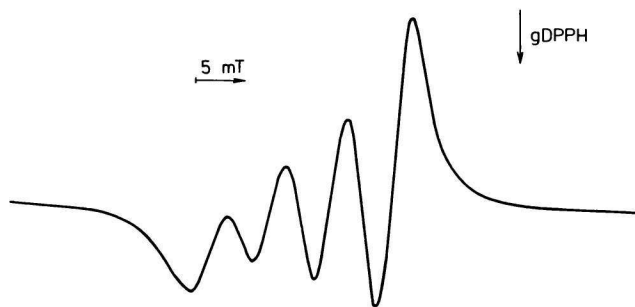


Fig. 3. EPR spectrum of aqueous solutions of the $\text{Cu(ida)} \cdot 2\text{H}_2\text{O}$, $[\text{Cu(ida)}_2]^{2-}$, and $\text{H}_2[\text{Cu(ida)}_4]^{4-}$ complexes.

does not appear. The spectra demonstrate the difference between the $[\text{Cu(ida)}_2]^{2-}$ and $[\text{Cu(ida)}_4]^{6-}$ complexes in the solid phase. The character of the spectrum also depends to a certain extent on the external cation, suggesting intermolecular interactions among paramagnetic atoms in the crystal structure. Aqueous solutions of all the studied complexes yield identical EPR spectra (Fig. 3). Splitting at copper nuclei only appears with a splitting constant of $a_{\text{Cu}} = 5.9 \text{ mT}$, indicating the predominant localization of an unpaired electron on the central copper atom. The g factor determined equals 2.13. Considerable asymmetry can be seen in the spectra. The EPR spectra unambiguously demonstrate that the complexes are converted in aqueous solutions into particles with the same surroundings of the central atom, regardless of the nature of the external cation or the value of α_{Cu} . This is also confirmed by the electronic spectra that are identical for all the studied substances.

However, this fact is not in agreement with the published stability constants for the Cu(II)—ida system [2—7]. It follows from the values of $\log \beta_1 = 10.57\text{—}10.63$ and $\log \beta_2 = 16.54\text{—}16.68$ (depending on the experimental conditions) that no significant changes in the composition of the complexes should occur on dissolution of solid 1:1 and 1:2 complexes. The composition and the stability constants in the Cu(II)—ida system were therefore reinvestigated with special emphasis on the possible formation of the 1:4 complex in solution which would explain the identical EPR spectra as being caused by the disproportionation of the $\text{M}_2[\text{Cu(ida)}_2]$ salts into the 1:1 and 1:4 complexes in solution, with marked preference for the 1:1 complex. The data obtained at $\alpha_{\text{Cu}} = 1:1, 1:2,$ and $1:4$ were treated statistically and the results are given in Table 3: The constants are generally in a good agreement with the published data [2—7]. Using the criteria recommended for the MINQUAD program [16], no significant amount of the 1:4 complex was detected in the system.

It is possible that isomerism and other solid-state effects are responsible for the discrepancy between the solution equilibria and the other properties of the

Table 3

Protonation constants of the ligand and stability constants
of the copper(II) complexes; L = ida²⁻

Constant (changes omitted)	log β (σ log β)	R factor/% [16]
[HL]/[H][L] [H ₂ L]/[H] ² [L]	9.328(5) 11.975(9)	0.78
[CuL]/[Cu][L] [CuL ₂]/[Cu][L] ²	10.54(1) 16.30(3)	0.60
[CuL]/[Cu][L] [CuL ₄]/[Cu][L] ⁴	10.54(3) 19.7(2)	2.92
[CuL]/[Cu][L] [CuL ₂]/[Cu][L] ² [CuL ₄]/[Cu][L] ⁴	10.54(1) 16.30(3) 21.3(1)	0.56 ^a

a) From the point of view of the criteria given in the text, this lowering of the R factor is insignificant when compared with the experimental errors in the region of possible existence of CuL₄.

substances. In the formation of the complexes with $\alpha_i = 1:4$, especially Ba₂H₂[Cu(ida)₄] · 12H₂O, polarization effect of the Ba²⁺ ion is more probably operative than the complexing effect of the bases [15], which, together with the lattice energy, prefers the formation of the 1:4 complex with probable coordination of four nitrogen atoms in the equatorial plane and of two water molecules in the axial position.

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Translated by M. Štulíková