

COMPLEXES OF UNIVALENT COPPER WITH ETHYLENEDITHIODIACETIC ACID*

J. PODLAHOVÁ

*Department of Inorganic Chemistry,
Charles University, 128 40 Prague 2*

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Univalent copper forms the complex anion CuZ_2^{3-} with ethylenedithiodiacetic acid ($\text{HOOCCH}_2\text{.SCH}_2\text{CH}_2\text{SCH}_2\text{COOH}$, H_2Z) with a stability constant of $10^{11.16}$. This ion was characterized in detail in solution and in its crystalline salts. It has been verified that the tetrahedral arrangement of CuS_4 with uncoordinated carboxyls, previously found in the H_3CuZ_2 acid by its crystal structure determination, is also characteristic for its salts in the solid state and in solution.

Thiopolycarboxylic acids, as sulphur analogues of complexones, exhibit very specific behaviour towards various types of cations. It has been found in previous works¹⁻⁵ that "hard" cations with a low affinity for thioetheric sulphur⁶ (*e.g.* Ca^{2+} , Mn^{2+} , lanthanoids, *etc.*) are only very weakly coordinated to these ligands ($\beta_1 \sim 10^2$). Interaction with cations from the end of the transition series, such as Ni^{2+} , Cu^{2+} , Cd^{2+} , is more pronounced ($\beta_1 \sim 10^5$). Among typical "soft" cations⁶, only divalent mercury has so far been studied^{3,7}; it forms stable complexes with thiopolycarboxylic acids (*e.g.* HgZ_2^{2-} , $\beta_2 = 10^{13.8}$).

Another important representative of the "soft" cations is univalent copper. The reaction of H_2Z with cuprous oxide and halides was investigated by Ramberg and Tiberg⁸; they prepared, among others, a compound to which they assigned the formula $\text{CuHZ.H}_2\text{Z}$, and its sodium salt. The crystalline structure of the former compound was recently determined⁹. Its characteristic structural feature is a tetrahedral arrangement of four sulphur atoms around a cuprous ion. The ligand carboxylic groups are not coordinated, but participate in intermolecular hydrogen bonding. James and Williams¹⁰ found potentiometrically that cuprous copper is markedly stabilized against oxidation in a H_2Z medium. Doležal and coworkers¹¹ studied the cuprous complex of H_2Z polarographically. They confirmed the existence of the CuZ_2^{3-} ion and determined an approximate value of its stability constant, $\beta_2 = 10^{11.1}$.

This work is intended to characterize the CuZ_2^{3-} complex anion more closely and especially to determine whether the coordination polyhedron is changed, with possible coordination of the carboxylic groups, during dissociation of the protons from H_3CuZ_2 .

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EXPERIMENTAL AND RESULTS

Chemicals

Ethylenedithiodiacetic acid was prepared from 1,2-dibromoethane and mercaptoacetic acid¹. The preparation with a purity of 99.8% had a m.p. of 109°C (literature⁸ value, 108–109°C). The other chemicals were *p.a.* substances from Lachema, Merck and Schering-Kahlbaum.

Instruments and Methods

The instrumentation used and the measuring and computing methods were described in previous papers^{1,2,5}. The IR-spectra in a region of 200–500 cm⁻¹ were measured on a Perkin-Elmer 325 instrument using the nujol mull method with polyethylene windows.

The ligand was determined by titration with nascent bromine³ after preliminary aerial oxidation of cuprous copper in an ammoniacal medium. Copper was titrated with EDTA after mineralization with hot nitric acid; lithium and sodium were determined by flame photometry and calcium manganometrically after separation as the oxalate. The water content was determined by drying over phosphorus pentoxide in a nitrogen atmosphere at 100 and 150°C.

Preparation of the Complexes

H₃CuZ₂: 1) according to work⁸ with subsequent recrystallization from hot water in the absence of air. The product had a melting point of 220–223°C (decomp.). 2) by reduction of divalent copper with the ligand: 0.50 g (2 millimol) of CuSO₄·5 H₂O and 2.10 g (10 millimol) of H₂Z were heated with 20 ml of water on a water bath. The sparingly soluble cupric complex, CuZ₂·2 H₂O, separated first¹; on further heating it dissolved and the solution became colourless.

TABLE I
Analytical Data for the Prepared Compounds

Compound (m.w.)	% Cu calc. (found)	% Z ²⁻ calc. (found)	% M calc. (found)	% H ₂ O calc. (found)
H ₃ CuZ ₂ (483.07)	13.15 (13.08)	86.22 (86.2)	0.63 (0.62) ^a	—
Li ₃ CuZ ₂ ·5 H ₂ O (590.95)	10.75 (10.73)	70.48 (69.7)	3.52 (3.5)	15.25 (15.61) ^b
Na ₃ CuZ ₂ ·10 H ₂ O (729.18)	8.71 (8.66)	57.12 (57.4)	9.36 (9.3)	24.71 (25.07) ^b
Ca ₃ (CuZ ₂) ₂ ·20 H ₂ O (1 440.66)	8.82 (8.96)	57.82 (57.6)	8.35 (8.44)	25.01 (25.18) ^c

^a Alkalimetric titration using phenolphthalein, ^b at 100°C, ^c at 150°C.

Within 1 hour white crystals separated from the cooling solution, which had a m.p. of 219 to 222°C (after recrystallization) and did not exhibit any depression in the melting point when mixed with sample (I). If an analogous reaction is carried out with excess cupric copper (10 : 1), the reaction mixture is alkalinized, CuO and Cu₂O are separated and the solution is acidified again, colourless crystals of bis-sulphone with a m.p. of 198–201°C (literature⁸ value, 200–202°C) can be isolated from the reaction mixture.

The sodium salt, Na₃CuZ₂·10 H₂O, was prepared according to the method of Ramberg and Tiberg⁸. The lithium and calcium salts, Li₃CuZ₂·5 H₂O and Ca₃(CuZ₂)₂·20 H₂O, respectively, were prepared by reaction of H₃CuZ₂ with an aqueous suspension of the equivalent amount of the appropriate carbonates at an elevated temperature and by crystallization. The preparations of all the salts were purified by recrystallization from aqueous ethanol in the absence of atmospheric oxygen.

Properties of the Substances

The analytical data are summarized in Table I. All the compounds are crystalline substances, yielding characteristic X-ray powder patterns, given in Table II. The X-ray pattern of H₃CuZ₂ is in very good agreement with the theoretical pattern calculated from the atomic coordinates^{9,12}.

TABLE II

Interplanar Distances and Line Intensities in X-ray Powder Patterns

Goniometric recording, CuK_α radiation. The hkl values for H₃CuZ₂ were calculated from the published structure⁹. D (Å)/I (hkl).

H₃CuZ₂: 7·89/30 (10 $\bar{1}$), 7·24/30 (101), 6·42/50 (011), 6·11/40 (110), 5·53/20 (11 $\bar{1}$), 5·29/5 (111), 4·95/20 (200), 4·66/5 (012), 4·33/5 (11 $\bar{2}$), 4·09/20 (112), 4·02/20 (21 $\bar{1}$), 3·86/100 (020), 3·61/25 (202, 103), 3·51/5 (21 $\bar{2}$), 3·46/25 (013), 3·40/5 (121), 3·35/5 (11 $\bar{3}$), 3·27/5 (212), 3·20/15 (022, 113), 3·10/20 (301, 12 $\bar{2}$), 3·04/15 (220), 3·02/5 (310), 2·98/5 (22 $\bar{1}$), 2·95/5 (21 $\bar{3}$), 2·90/5 (221, 004), 2·74/15 (22 $\bar{2}$, 213), 2·61/5 (312), 2·57/15 (20 $\bar{3}$, 030, 114), 2·51/10 (031, 320), 2·48/5 (31 $\bar{3}$, 32 $\bar{1}$, 400), 2·40/35 (204, 303), 2·36/5 (32 $\bar{2}$), 2·31/5 (024), 2·25/5 (322, 23 $\bar{1}$, 41 $\bar{2}$), 2·22/5 (124, 231, 105), 2·18/5 (31 $\bar{4}$), 2·13/5 (033, 115), 2·02/10 (330, 421), 1·982/10 (30 $\bar{5}$, 50 $\bar{1}$, 331), 1·926/45 (040), 1·867/10 (134, 511, 51 $\bar{2}$), 1·824/5 (23 $\bar{4}$, 305), 1·792/15 (240, 142), 1·749/5 (206), 1·726/15 (24 $\bar{2}$, 026, 12 $\bar{6}$, 41 $\bar{5}$), 1·648/20 (325, 522, 600), 1·606/10 (243, 044), 1·580/5 (433, 21 $\bar{7}$, 342);

Li₃CuZ₂·5 H₂O: 13·5/50, 9·5/25, 6·7/100, 5·94/20, 4·43/50, 4·27/30, 3·58/20, 3·32/5, 3·12/10, 2·98/15, 2·84/5, 2·64/35, 2·51/20, 2·42/15, 2·27/10, 2·20/10, 2·17/10, 2·09/5, 2·04/5, 1·882/5, 1·866/10, 1·798/5, 1·734/5, 1·648/5, 1·631/5, 1·578/5, 1·429/5.

Na₃CuZ₂·10 H₂O: 13·0/15, 7·1/15, 6·6/70, 5·67/5, 5·46/10, 5·04/5, 4·72/5, 4·66/5, 4·35/20, 4·07/5, 3·67/10, 3·41/5, 3·27/10, 3·19/5, 3·09/5, 3·03/10, 2·95/5, 2·82/5, 2·70/5, 2·61/100, 2·54/5, 2·46/5, 2·37/5, 2·26/5, 2·18/50, 2·14/5, 2·06/5, 2·03/5, 1·949/10, 1·869/15, 1·809/5, 1·766/5, 1·701/10, 1·634/20, 1·509/5, 1·439/5, 1·352/5, 1·307/5.

Ca₃(CuZ₂)₂·20 H₂O: 10·6/45, 9·2/5, 6·14/20, 5·71/40, 5·24/100, 4·58/45, 4·29/10, 4·04/10, 3·91/10, 3·68/10, 3·54/20, 3·48/35, 3·35/10, 3·00/10, 2·83/20, 2·81/15, 2·69/10, 2·61/20, 2·51/5, 2·31/5, 2·27/5, 2·23/5, 2·12/10, 2·12/10, 2·09/40, 2·02/10, 1·953/10, 1·892/10, 1·845/10, 1·777/5, 1·666/5, 1·637/5, 1·493/10.

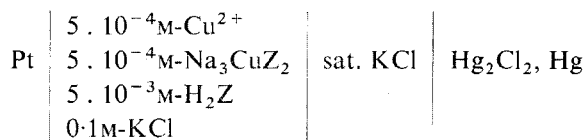
All the substances are diamagnetic and exhibit an intense band at 250 ± 3 nm in their diffuse reflectance spectra. The H_3CuZ_2 acid is sparingly soluble in water, but the salts are readily soluble. Aqueous solutions are slowly oxidized by atmospheric oxygen to divalent copper. Reactions in which the IR-spectra differ from that of the free ligand (H_2Z or Na_2Z), are summarized in Table III.

Study of Aqueous Solutions

Solution preparation and all measurements were carried out in the absence of atmospheric oxygen.

Stability Constant

The dependence of the redox potential of the $Cu(II)Z/Cu(I)Z_2^{3-}$ system on the pH was studied at $25 \pm 0.1^\circ C$. The following cell with liquid junction was employed:



The value of the liquid junction potential was determined from measurements in the absence of the ligand and from comparison with the tabulated potential value for the $Cu(I)/Cu(II)$ system in a chloride medium¹³. The pH was varied by adding solutions of HCl or KOH in 0.1M-KCl.

The potential dependence on the pH is given in Fig. 1. Only chloro complexes are present in the system in a strongly acidic region ($pH < 1.5$), as follows from the potential value, which is identical with the tabulated value for this medium. In the region, $pH 1.5 - 3$, at the given component concentrations, complexes $Cu(II)Z$, $Cu(II)HZ^+$ (ref.¹) and $H_nCu(I)Z_2^{n-3}$ (ref.⁷) are gradually formed and their stability is substantially higher than that of the chloro complexes. A slow increase in the poten-

TABLE III

Selected Bands from the IR-Spectra

m = medium, vs = very strong, w = weak, vw = very weak, s = strong, b = broad.

Compound	$\nu(Cu-S)$	$\nu(C-S)$	$\nu_a(COO)$	$\nu(O-H \cdots O)$	$\nu(H_2O)$
H_3CuZ_2	397 m	639 m 651 w	1 712 vs	2 460 vw 2 545 w 2 655 w	—
$Li_3CuZ_2 \cdot 5 H_2O$	396 m	649 w	1 610 vs	3 200 m, b	3 410 s, b
$Na_3CuZ_2 \cdot 10 H_2O$	394 m	641 w	1 608 vs	3 340 s, b	3 465 vs
$Ca_3(CuZ_2)_2 \cdot 20 H_2O$	392 m	642 w	1 592 vs	3 250 m, vb	3 400 s, vb

tial up to pH 4 reflects a stepwise dissociation of protons from the hydrogen complexes and the potential is constant in the range, pH 4–6.5. Then a decrease occurs due to decomposition of the cupric complex to give cupric hydroxide.

The Peters formula applied to the constant potential value found between pH 4 and 6.5 assumes the form (the charges are omitted)

$$E = E_0 + 0.0591 \log \frac{\beta_{\text{Cu(I)Z}_2}}{\beta_{\text{Cu(II)Z}}} + 0.0591 \log \frac{[\text{Cu(II)Z}]}{[\text{Cu(I)Z}_2]} + 0.0591 \log [Z],$$

where $E_0 = +0.153 \text{ V}$ (ref.¹³), the third term is zero (in the presence of excess ligand $[\text{Cu(II)Z}] = [\text{Cu(I)Z}_2]$) and $[Z] = c_Z - 2c_{\text{Cu(I)}} - c_{\text{Cu(II)}} = 4.5 \cdot 10^{-3} \text{ M}$. At pH = 4.5–6.5, $E = +0.481 \pm 0.001_5 \text{ V}$ and the stability constant, $\beta_{\text{Cu(II)Z}}$ is (ref.¹) $10^{5.68 \pm 0.03}$. From these values it follows for the stability constant of ion Cu(I)Z_2^{3-} that

$$\beta_2 = \frac{[\text{CuZ}_2]}{[\text{Cu}][\text{Z}]^2} = 10^{11.16 \pm 0.04}$$

Dissociation Constants of H_3CuZ_2

It is evident from alkalimetric titration of $1 \cdot 10^{-3} \text{ M-H}_3\text{CuZ}_2$ with sodium hydroxide, carried out in a 0.1 M-NaClO_4 medium at $25 \pm 0.1^\circ \text{C}$ (Fig. 2), that protons dissociate

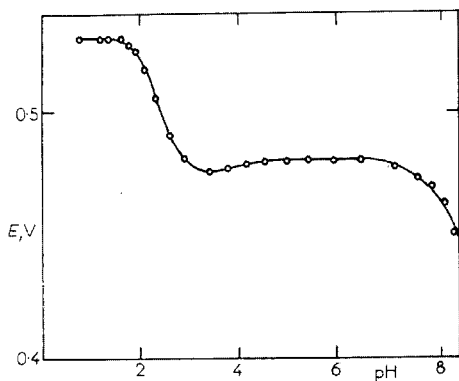


FIG. 1
Dependence of the Redox Potential of the $\text{Cu(II)Z/Cu(I)Z}_2^{3-}$ System on the pH in a 0.1 M-KCl Medium

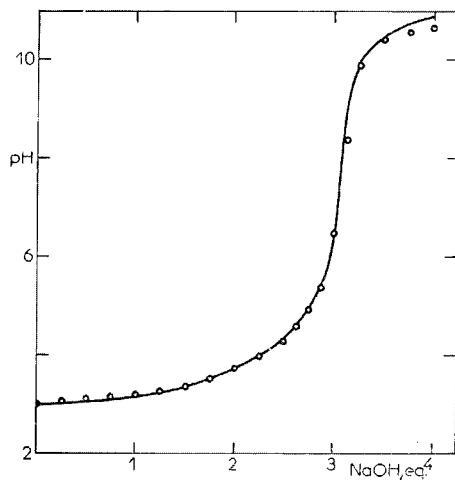


FIG. 2
Titration of $1 \cdot 10^{-3} \text{ M-H}_3\text{CuZ}_2$ with 0.02 M-NaOH Solution in a 0.1 M-NaClO_4 Medium

from the complex acid simultaneously in a single buffering step. The values of the acid-base dissociation constants were calculated by statistical analysis of the titration curve employing the SCOGS program¹⁴. It was verified during the computation that the dissociation of the complex anion is negligible at stability constant $10^{11.16}$ (fraction $\sum_{i=0}^{i=2} [H_iZ]$ is less than 1% of the analytical concentration of Z in the whole pH range). The dissociation constant values amount to

$$pK_1 = 2.95 \pm 0.02; \quad pK_2 = 3.19 \pm 0.02; \quad pK_3 = 4.20 \pm 0.03.$$

Spectra in Aqueous Solutions

The IR-spectrum of a Na_3CuZ_2 solution in deuterium oxide is characterized by maxima at 1390 and 1605 cm^{-1} in the region of carboxyl stretching vibrations, which are thus essentially identical with the bands obtained with the crystalline substances.

The UV-spectrum of a Na_3CuZ_2 solution exhibits a single charge-transfer maximum at 248 nm ($\epsilon_M = 5700$) which is also identical with the diffuse reflectance spectrum of the acid and its salts. The band intensity is constant in a pH range of 3–9. The band intensity decreases somewhat at extreme pH values, but decomposition of the complex to give cuprous oxide occurs only after prolonged standing of a strongly alkaline solution.

DISCUSSION

The coordination types found so far for thiopolycarboxylic acids can be classified into three groups: 1) bonding exclusively through carboxyls with "hard" ions, such as Ca^{2+} and early elements of the first transition series^{1,5}; 2) bonding exclusively through sulphur atoms with typical "soft" ions, e.g. in compounds $H_2Hg \cdot ZX_2$ ($X = \text{halogen}$)³ and in the complexes of cuprous copper studied in the present paper; 3) bonding through both carboxyls and sulphur with most other metal ions. The stability of the metal-sulphur bond can vary in a rather wide range with these compounds and is reflected in their properties, especially in the thermodynamic stability and charge-transfer spectra. Complexes of thiopolycarboxylic acids whose crystal structures are known provide a good example: $ZnS(CH_2COO)_2 \cdot 4 H_2O$ ($Zn-S$ 2.60 Å (ref.¹⁵), $\log \beta_1 = 3.30$ (ref.³)), $NiZ \cdot 2 H_2O$ ($Ni-S$ 2.46 Å (ref.¹⁶), $\log \beta_1 = 4.49$ (ref.¹)) and H_3CuZ_2 ($Cu-S$ 2.32 Å (ref.⁹), $\log \beta_2 = 11.16$). It is important for considerations on the structure of the complexes of univalent copper with H_2Z that the electronic and IR-spectra of the acid and its salts are virtually identical in the solid state and in solution. The wave number of the carboxyl anti-symmetrical stretching vibration corresponds to that for uncoordinated $-COO^-$, or $-COOH$, groups and the $\nu(C-S)$ vibration band is shifted towards lower wave

numbers in agreement with strong coordination of sulphur. A band corresponding to the Cu—S stretching vibration also appears in the spectra at $395 \pm 3 \text{ cm}^{-1}$; its position agrees with the value calculated from the Badger rule¹⁷ for a single Cu—S bond 2.32 \AA in length.

It is important for the behaviour of the CuZ_2^{3-} ion in solution that the redox potential varies very little in the region of protonation of this ion. It is further apparent from the dissociation constants of H_3CuZ_2 that the protons are only slightly acidic compared with H_2Z (ref.¹). The stability constant for the CuZ_2^{3-} ion, determined here from measurement of the redox potential, is in very good agreement with the value determined earlier polarographically. The complex anion is stable in a very broad pH range.

It can be concluded that the complex anion of univalent copper with ethylenedithiodiacetic acid, CuZ_2^{3-} , is a stable unit, from the thermodynamic as well as the redox aspect. It is evident that the tetrahedral coordination of four sulphur atoms around the central copper ion remains preserved in this anion under all conditions. Poorly pronounced changes in the properties during acid-base dissociation reflect the fact that the carboxylic groups are not coordinated.

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