Coordination Chemistry of Lipoic Acid and Related Compounds, Part 1  
Syntheses and Crystal Structures of the UV- and Light-Sensitive Lipoato Complexes \[M(\text{lip})_2(\text{H}_2\text{O})_2]\ (M = \text{Zn, Cd})

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Lipoic Acid, Carboxylate Coordination, Zinc(II) Complex, Cadmium(II) Complex, X-Ray

The rac-lipoato (lip\textsuperscript{−}) complexes \[\text{Zn(lip)}_2(\text{H}_2\text{O})_2\] (1) and \[\text{Cd(lip)}_2(\text{H}_2\text{O})_2\] (2) were obtained in good yields from solutions of sodium lipoate and the respective metal nitrate in methanol/water. 1 and 2 form pale yellow, moderately light-sensitive crystals.

Both compounds were structurally characterized by single-crystal X-ray diffraction. 1: C2/c, \[a = 39.958(6), b = 5.360(1), c = 10.794(1) \text{ Å}, \beta = 95.76(1)^{\circ}, Z = 4, wR_2 = 0.150 \text{ (all data)}\]. 2: C2/c, \[a = 38.200(2), b = 5.472(1), c = 11.179(1) \text{ Å}, \beta = 92.72(1)^{\circ}, Z = 4, wR_2 = 0.090 \text{ (all data)}\]. The metal ions are hexacoordinated by the oxygen atoms of two chelating carboxylate ligands and two aqua ligands. The crystal structures are very similar but not isotypic. They are layer structures, in which the complexes within a layer are interconnected by a network of hydrogen bonds. Adjacent layers have contacts via the 1,2-dithiolanyl rings of their lipoato ligands.

Crystals of 1 and 2 decompose on exposure to visible light or ultraviolet radiation in the 280–390 nm range. Photopolymerization by formation of intermolecular S-S bonds is very probably involved. Furthermore, the infrared spectra reveal the transformation of COO\textsuperscript{−} into COOH groups.

Introduction

Lipoic acid (\(\alpha\)-lipoic acid, thioctic acid, 5-(1,2-dithiolan-3-yl)pentanoic acid, Hlip) \[1\] is a coenzyme of several biological group transfer reactions \[2, 3\]. The native form has the \(R\) configuration. Racemic lipoic acid is used as a medicinal drug in the treatment of diabetic polyneuropathy, a complication induced by diabetes \[4, 5\].

In the enzyme-bound state of lipoic acid, the carbonyl group is joined via an amide linkage to the amino group of a lysine side chain \[6\]. Thus, the carbonyl end of the molecule becomes more or less inert to metal ion coordination, leaving the five-membered ring as the only active part. The disulfide bond can be easily reduced, and the resulting dithiol is a probable target of toxic species like Hg\textsuperscript{2+}, RHg\textsuperscript{+} and RA\textsubscript{S2+} \[7\]. Immediately after the biosynthesis \[8\] and during therapeutic applications of lipoic acid, however, the carboxylate group, too, should be accessible to metal ions. It was shown that the stability of 1:1 complexes of lipoate (lip\textsuperscript{−}) with biologically important metal ions (\(e.g. Cu\textsuperscript{2+} \text{ and Zn}\textsuperscript{2+}\)) is solely determined by carboxylate coordination; but the results did not exclude \textit{weak} M\textsuperscript{2+}-disulfide interactions \[9\]. To our knowledge, no detailed account of the preparation or crystal structure of a lipoato complex has appeared. The X-ray structure of \[\text{Zn(lip)}_2(\text{H}_2\text{O})_2\] was briefly described by Dubler \textit{et al.} in a conference abstract \[10\].

Another notable property of lipoic acid is its photosensitivity \[11, 12\]. On exposure to ordinary light, ring opening and polymerization via formation of intermolecular S-S bonds occur. Solution studies revealed a distinct influence of the solvent \[13\]. Possible technical applications exist for photosensitive...
coatings that contain lipoic acid as the reactive component [14].

In the present paper we report a high-yield synthesis of the lipoato complexes [Zn(lip)\(_2\)(H\(_2\)O)\(_2\)] and [Cd(lip)\(_2\)(H\(_2\)O)\(_2\)]. The crystal and molecular structures and the solid-state photodecomposition of both compounds are discussed.

**Experimental**

All chemicals were purchased from commercial sources, except for racemic lipoic acid, which was kindly provided by ASTA Medica AG. Infrared spectra were obtained on an FT-IR spectrometer Bio-Rad FTS 710. A Philips PW 1710 automated powder diffractometer system (CuK\(_\alpha\) radiation) was used to check the crystallinity of irradiated samples. A sample of the cadmium complex was exposed to intense synchrotron radiation of 12.9 keV (corresponding to \(\lambda = 0.96 \) Å) at the European Molecular Biology Laboratory at HASYLAB (DESY, Hamburg). Elemental analyses were performed by the Microanalytical Laboratory Beller, Göttingen, Germany.

**Caution!** Cadmium compounds are highly toxic and probably carcinogenic. They should be handled with care to avoid exposure. To avoid health hazards by intense UV radiation, suitable precautions should be taken, e. g. by wearing protective glasses.

**Preparation of compounds**

\[[Zn(lip)\(_2\)(H\(_2\)O)\(_2\)] (1): 2.06 g (10.0 mmol) of rac-lipoic acid was dissolved in 250 ml of methanol. To the stirred solution were added 0.40 g (10.0 mmol) of sodium hydroxide in 75 ml of water and 1.49 g (5.0 mmol) of Zn(NO\(_3\))\(_2\) · 6 H\(_2\)O in 250 ml of methanol. The reaction mixture was allowed to stand undisturbed and light-protected in a crystallizing dish. During the next few days the solvent vaporized almost completely, and 1 crystallized as pale yellow, elongated plates. The product was isolated on a large-pored glass filter, thoroughly washed with water to remove sodium nitrate, and dried in vacuo. It was stored in the dark. Yield 2.09 g (82%).

\[C\(_{16}\)H\(_{30}\)O\(_9\)S\(_2\)Zn\] (512.1)

Calcd C 37.53 H 5.90 S 25.05 Zn 12.77%.

Found C 37.38 H 5.91 S 25.02 Zn 12.74%.

IR (KBr): 3160 s br (OH), 2926 s (CH), 1543 vs (COO\(^{-}\)), 1443 s, 1410 s, 727 m cm\(^{-1}\).

\[[Cd(lip)\(_2\)(H\(_2\)O)\(_2\)] (2): The preceding method was used with 1.54 g (5.0 mmol) of Cd(NO\(_3\))\(_2\) · 4 H\(_2\)O. The crystals obtained had the same color and shape as those of compound 1. As in the case of 1, unnecessary exposure to light was avoided. Yield 2.38 g (85%).

\[C\(_{16}\)H\(_{30}\)CdO\(_{6}\)S\(_2\)] (559.1)

Calcd C 34.37 H 5.41 Cd 20.11 S 22.94%.

Found C 34.34 H 5.35 Cd 19.80 S 22.72%.

**UV and visible-light irradiation**

In a typical experiment a 0.5-g sample of polycrystalline 1 or 2 was placed into a quartz tube (180 mm length, 13 mm inner diameter), which was flushed with pure nitrogen and sealed. The sample was distributed over the largest possible area within the tube. A UV lamp Bioblock Scientific VL-6M (6 W - 312 nm tube), whose radiation covered the 280-390 nm range, was used. The distance between the sample and the filter of the lamp was 4 cm. An intensity of 0.68 mW/cm\(^2\) at a distance of 15 cm from the filter is specified by the German supplier (Novodirect GmbH). During the experiment the sample was protected against visible light. A temperature of 25±2 °C was maintained by air cooling.

A 100-W tungsten filament lamp was used to prove the light sensitivity of 1 and 2. A porcelain crucible covered with a UV filter served as sample container. The lamp was positioned 12 cm above the sample. Air cooling ensured a temperature of 27±2 °C.

**X-ray structure determinations**

Suitable single crystals of 1 and 2 were obtained from preparations very similar to those described above. The crystals were sealed into thin-walled glass capillaries and mounted on a Siemens/STOE AED2 automated four-circle diffractometer (MoK\(_\alpha\) radiation). Accurate lattice parameters of 1 and 2 were determined by centering 30 and 36 reflections, respectively, including Friedel pairs. The crystal data are summarized in Table I together with information pertaining to data collection and structure refinement. The intensity data were collected by the \(\omega-2\theta\) step scan technique at 24±1 °C. At the end of data collections the intensity variations were −3% (1) and −35% (2). In addition to the usual corrections, an empirical absorption correction (\(\psi\)-scan) was applied to the data set of 1.

The structure of 1 was solved by using the atomic coordinates of 2 as starting parameters (for the metal atom, O(1), O(2), O(3), C(6), C(7), and C(8)). The structure of 2 had been solved before by direct methods (program SHELXS-86 [15]). Both structures were refined by standard least-squares and Fourier techniques, at first on F (SHELX-76 [16]) and finally on F\(^2\) (SHELXL-93 [17]). All non-hydrogen atoms, except S(2b), were refined anisotropically. Hydrogen atoms were given U values 1.5 (H\(_2\)O) and 1.2 times (CH, CH\(_2\)), respectively, the equivalent isotropic displacement factors \(U_{eq}\) of the atoms to which they were attached. The positions of the H atoms of...
Empirical formula: $\text{C}_{496}\text{H}_{802}\text{O}_{18}\text{S}_{8}\text{Zn}$

Formula weight: 512.06

Crystal system: monoclinic

Space group: C2/c

a [Å]: 39.958(6)
b [Å]: 5.360(1)
c [Å]: 10.794(1)
$\beta$ [°]: 95.76(1)
V [Å³]: 2300.1(6)

$Z$: 4

d_calc [g cm$^{-3}$]: 1.479

Crystal dimensions [mm]: 1.37x0.48x0.06

$\mu$(MoK$\alpha$) [cm$^{-1}$]: 14.58

$2\theta$ limits [°]: 4 < $2\theta$ < 48

Index ranges: 0 < h < 45, 0 < k < 6, 0 < l < 12

Total no. reflections: 1835

Independent reflections: 1807

Reflections with I > 2$\sigma$(I): 1580

Parameters: 132

Goodness-of-fit on $F^2$: R$_{int}$ = 0.0092

$R$ indices$^a$ (all data): R = 0.0617

wR$^2$ = 0.0179

Largest shift/e.s.d. in final refinement cycle: 0.000

Max/min electron density in final difference map (eÅ$^{-3}$): +0.75/−0.53

Results and Discussion

Synthesis and infrared spectra

The compounds [Zn(lip)$_2$(H$_2$O)$_2$] (1) and [Cd(lip)$_2$(H$_2$O)$_2$] (2) were obtained from the reaction of the respective metal nitrates with racemic lipoate; the latter was prepared in situ from lipoic acid and sodium hydroxide:

\[\text{M(NO}_3)_2 + 2 \text{Hlip} + 2 \text{NaOH} \rightarrow \text{M(lip)}_2(\text{H}_2\text{O})_2 + 2 \text{NaNO}_3\] (M = Zn, Cd)

The use of a methanol/water mixture as reaction medium and relatively low initial concentrations (9 mM M$^{2+}$) proved to be favorable. Slow evaporation of the solvents led to analytically pure, coarse-crystalline products in good yields (> 80%). Once they are crystallized, 1 and 2 are insoluble both in methanol and in water. They are also sparingly soluble in most other organic solvents, except dimethyl sulfoxide.

The infrared spectra are dominated by strong and broad $\nu$(O-H) bands in the 3200 cm$^{-1}$ region and by very strong bands at 1543 (1) and 1532/1516 cm$^{-1}$ (2), respectively, which are caused by the antisymmetric stretching vibration of the COO$^-$ groups. Absorptions at 1443 (1) and 1458/1445 cm$^{-1}$ (2) are very probably due to the symmetric COO$^-$ vibrations.
Table II. Bond lengths [Å] and angles [°] in the MO₆ coordination units of the [M(lip)₂(H₂O)₂] complexes 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>M = Zn (1)</th>
<th>M = Cd (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-O(1)</td>
<td>2.164(3)</td>
<td>2.337(3)</td>
</tr>
<tr>
<td>M-O(2)</td>
<td>2.236(4)</td>
<td>2.344(3)</td>
</tr>
<tr>
<td>M-O(3)</td>
<td>2.015(3)</td>
<td>2.225(3)</td>
</tr>
<tr>
<td>O(1)-M-O(2)</td>
<td>58.8(1)</td>
<td>55.5(1)</td>
</tr>
<tr>
<td>O(1)-M-O(3)</td>
<td>102.0(1)</td>
<td>102.8(1)</td>
</tr>
<tr>
<td>O(1)-M-O(1')</td>
<td>161.6(2)</td>
<td>161.5(2)</td>
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<tr>
<td>O(1)-M-O(2')</td>
<td>106.5(1)</td>
<td>109.5(1)</td>
</tr>
<tr>
<td>O(1)-M-O(3')</td>
<td>89.9(1)</td>
<td>89.3(1)</td>
</tr>
<tr>
<td>O(2)-M-O(3)</td>
<td>95.4(1)</td>
<td>97.8(1)</td>
</tr>
<tr>
<td>O(2)-M-O(2')</td>
<td>86.2(2)</td>
<td>87.4(1)</td>
</tr>
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<td>O(2)-M-O(3')</td>
<td>147.4(1)</td>
<td>143.7(1)</td>
</tr>
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<td>O(3)-M-O(3')</td>
<td>100.2(2)</td>
<td>98.7(2)</td>
</tr>
</tbody>
</table>

a Symmetry transformation used to generate equivalent atoms: 1 - x, y, 1.5 - z.

stretching modes. On UV irradiation (see below) these bands lose intensity to about the same degree as the νₛ(COO⁻) bands. In the relevant spectral region no other bands show this behavior. The observed energy differences between νₐ(COO⁻) and νₛ(COO⁻), namely 100 (1) and ca. 73 cm⁻¹ (2), respectively, indicate the presence of chelating carboxylate groups [18]. This corresponds with the results from the X-ray structure determinations.

Crystal and molecular structures

Crystals of 1 and 2 consist of discrete [M(lip)₂(H₂O)₂] complexes. Each complex is located on a crystallographic 2-fold rotation axis. Therefore its two lip⁻ ligands have the same configuration. In Figs. 1 and 2 the R configured ligands are depicted as the major forms (with S(2a) and S(2a')). As a consequence of the space group symmetry, the crystals contain racemic mixtures.

The metal ions are hexacoordinated by the oxygen atoms of two chelating lip⁻ carboxylate ligands and two aqua ligands. Metrical data of the inner coordination spheres are given in Table II. The binding mode of the carboxylate groups is asymmetric in the case of 1 (dₘ⁻(O=O) = 0.072 Å), while in the cadmium complex 2 the carboxylate is bonded asymmetrically. The aqua ligands are in a cis arrangement. In a given complex, the M-OH₂ bonds are considerably shorter than the M-O₂C bonds. The coordination polyhedra are severely distorted from ideal geometries. This can mainly be attributed to the small intra-chelate angles O(1)-M-O(2) measuring 58.8(1) and 55.5(1°) in 1 and 2, respectively. The bond distances and selected angles of the ZnO₆ group of 1 from another X-ray structure determination were reported in ref. [10]. The values given there agree with ours within four times the e. s. d. or better. A few other zinc complexes of the type [Zn(η²-O₂CR)₂(H₂O)₂], to which 1 belongs, are known; they show the same structural features of the ZnO₆ group as 1 (see e. g. refs. [19 - 22]).

The fact that the Zn²⁺ ion prefers lower coordination numbers than Cd²⁺ is statistically well-proven [23]. For coordination by oxide and o xo anions, average coordination numbers of 4.90 (Zn²⁺) and 6.26 (Cd²⁺) have been observed [24]. Another survey, which additionally included anionic fluorine donors, arrived at average coordination numbers of 4.98 (Zn²⁺) and 6.14 (Cd²⁺) [25]. This trend is also found in compounds having the general composition of 1 and 2, namely M(O₂CR)₂ · 2 H₂O. With
Table III. Bond distances [Å] and angles [°] of the lipoate moieties in the complexes 1 and 2 and in lipoic acid (Hlip)

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>Hlip [37]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-S(2)</td>
<td>2.056(3)</td>
<td>2.047(3)</td>
<td>2.053(4)</td>
</tr>
<tr>
<td>S(1)-C(1)</td>
<td>1.785(9)</td>
<td>1.789(8)</td>
<td>1.79(1)</td>
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<tr>
<td>S(2)-C(3)</td>
<td>1.817(8)</td>
<td>1.791(7)</td>
<td>1.83(1)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.451(10)</td>
<td>1.484(9)</td>
<td>1.51(2)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.435(11)</td>
<td>1.446(9)</td>
<td>1.55(2)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.422(9)</td>
<td>1.429(8)</td>
<td>1.53(1)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.504(11)</td>
<td>1.497(8)</td>
<td>1.51(1)</td>
</tr>
<tr>
<td>C(5)-C(6)</td>
<td>1.531(10)</td>
<td>1.484(8)</td>
<td>1.53(1)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.402(10)</td>
<td>1.489(7)</td>
<td>1.55(1)</td>
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<tr>
<td>C(7)-C(8)</td>
<td>1.512(8)</td>
<td>1.505(6)</td>
<td>1.50(1)</td>
</tr>
<tr>
<td>C(8)-O(1)</td>
<td>1.251(6)</td>
<td>1.259(5)</td>
<td>1.20(1)</td>
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<tr>
<td>C(8)-O(2)</td>
<td>1.259(5)</td>
<td>1.259(5)</td>
<td>1.31(1)</td>
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<td>C(2)-C(3)</td>
<td>1.512(7)</td>
<td>1.516(6)</td>
<td>1.429(8)</td>
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<tr>
<td>C(3)-C(4)</td>
<td>1.422(9)</td>
<td>1.429(8)</td>
<td>1.53(1)</td>
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<tr>
<td>C(4)-C(5)</td>
<td>1.497(8)</td>
<td>1.489(7)</td>
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<td>C(5)-C(6)</td>
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<td>C(8)-O(2)</td>
<td>1.259(5)</td>
<td>1.259(5)</td>
<td>1.31(1)</td>
</tr>
</tbody>
</table>

a In 1 and 2 the atom S(2) is disordered (see text), and the main split position S(2a) is given as S(2) in the Table.

M = Zn coordination numbers of 6 (see above), 5 [26], and 4 [27, 28] occur; intermediate forms with [4+2] coordination, i.e., with two secondary Zn-O-C bonds, are known [29]. In the cadmium analogues the metal ion frequently tends to adopt higher coordination numbers, e.g., 7 [30, 31], which are rendered possible by bridging carboxylate ligands. Thus a pair of zinc and cadmium carboxylates like 1 and 2 showing the same composition and essentially the same coordination geometry is rather exceptional.

In crystals of 1 and 2 each complex forms eight hydrogen bonds to four neighboring molecules (see Fig. 3). Due to the crystallographic symmetry, only two different hydrogen bonds occur. Their metrical data in 1 are: O(3)--O(1III) 2.737, O(3)-H(1w) 0.83(4), O(1III)--H(1w) 1.91 Å, O(3)-H(1w)--O(1III) 170°, and O(3)--O(2II) 2.698, O(3)-H(2w) 0.83(4), O(2II)--H(2w) 1.87 Å, O(3)-H(2w)--O(2II) 171°. The corresponding values for 2 are: 2.724, 0.77(4), 1.96 Å, 177°, and 2.720, 0.77(4), 1.97 Å, 165°. O(1III) and O(2II) are generated by the symmetry transformations x, −y, z−0.5 and x, y−1, z, respectively. The distances and angles are typical of HO-H⋯O hydrogen bonds [32, 33]. A comparison of the metrical data clearly shows that there are only minor differences between the hydrogen-bonding networks in these two compounds. The networks are two-dimensional and parallel to the b,c plane. The strong interconnection of the complexes by hydrogen bonds may cause the low solubilities in solvents in which lipoic acid easily dissolves (e.g., methanol and tetrahydrofuran).

The crystal structures of 1 and 2 are very similar in many respects. This applies to the lattice parameters, the atomic coordinates of half of the non-hydrogen atoms and the hydrogen-bonding patterns (see above). Different bends of the ligand chains at the C(6) atoms, however, result in different positions of the peripheral atoms, including those of the 1,2-dithiolanyl rings. This is shown in Fig. 4. The atom pairs labeled there have been used to calculate a best fit of the central parts of the complexes 1 and 2 (OFIT instruction in the XP package of the SHELXTL PC program [34]). A maximum distance of only 0.26 Å between a core atom of 1 and its...
Fig. 4. Comparison of the molecular shapes of 1 (dashed lines) and 2 (solid lines). The S(2b), S(2b') and H atoms have been omitted.

Fig. 5. Packing diagrams for the compounds [M(lip)_2(H_2O)_2].

counterpart in 2 was obtained; the unweighted root-mean-square distance was 0.17 Å. Due to the strong deviations of the peripheries of the complexes, the crystal structures of 1 and 2 cannot be termed isotypic. Instead they are homeotypic [35].

Both compounds form layer structures. Complexes of adjacent layers interact with each other only by van der Waals forces between their 1,2-dithiolanyl rings (see Fig. 5). The shortest intermolecular S···S contacts exist between the layers: S(1)···S(1^IV) 3.970 Å in 1 (1.5 - x, 1.5 - y, 3 - z) and S(1)···S(1^IV) 3.541 Å in 2 (1.5 - x, 1.5 - y, 1 - z). The van der Waals distance is 3.6 Å [36]. These S···S contacts may play an essential role in the photodecomposition described below. There are striking similarities between the crystal structures of the compounds [M(lip)_2(H_2O)_2] and [Zn(bta)_2(H_2O)_2] (bta^- = (benzylthio)acetate) [20]. The space group is always C2/c, and the lattice parameters differ by only 3 to 6%. Even the shape of the bta^- ligand in the zinc complex is reminiscent of the bent lip^- ligand in 2.

At present, metrical data of the lipoate moiety are only known for three compounds, namely lipoic acid [37] and the metal complexes 1 and 2. These data are compiled in Table III. One result is that a value of 2.05 ± 0.01 Å for the S-S bond length in the 1,2-dithiolanyl ring of lip^- could be established by three separate structure determinations. This value is unexceptional and does not reflect the tendency of this bond to be easily cleaved by reduction. It compares with the mean S-S bond distance of 2.05(3) Å that was calculated on the basis of 99 C-S-S-C fragments studied by X-ray diffraction [38].

Some bond distances and angles in the lip^- ligands of 1 and 2 are apparently affected by slight disorders which could not be described as such. The atoms concerned are C(3) and C(7). C(3) belongs to the 1,2-dithiolanyl ring and is bonded to S(2), which could be refined satisfactorily on two split positions (see Experimental). We interpret this latter disorder as caused by the occasional presence of the 'wrong' enantiomer.

Ultraviolet and light sensitivity

Crystals of 1 and 2 are moderately sensitive to UVB (280 - 320 nm) and UVA (320 - 400 nm) radiation and to visible light as well. Under the conditions described above (see Experimental), first signs of decomposition by UV or light irradiation were observed after one day and one week, respectively. On the other hand, the compounds are thermally stable at least up to 60 °C: light-protected samples that were kept at this temperature under an N_2 atmosphere did not change over a one-week period. During X-ray data collection of 2, the crystal showed a considerable deterioration. This prompted us to examine the possibility of inducing chemical reactions by high-energy electromagnetic radiation. For this purpose, a polycrystalline sample of 2 was exposed to very intense 12.9-keV synchrotron radiation for 2 h. The infrared spectrum of the irradiated sample indicated, however, that no chemical changes had taken place.

There are various methods of detecting the UV- and light-induced decomposition of 1 and 2 and of monitoring its progress:
(i) Rather early the colors change from pale yellow to yellowish brown (1) and light brown (2), respectively.

(ii) Products are formed that, in contrast to 1 and 2, are insoluble in dimethyl sulfoxide. Their amount increases with longer irradiation times.

(iii) The crystal structures break down. After prolonged UV irradiation samples of 1 and 2 are entirely and almost amorphous, respectively, as is evidenced by their X-ray powder diffraction diagrams. New crystalline phases do not occur.

(iv) In the infrared spectra the most remarkable of the numerous changes caused by irradiation are the decrease of the $\nu$(COO$^-$) and the $\nu$(O-H) absorptions and the appearance of a new band at 1705 cm$^{-1}$. During the UV irradiation experiment described under Experimental the 1705-cm$^{-1}$ band became the strongest one after two weeks and increased still further.

The two compounds do not differ significantly with respect to the rate and the character of the decomposition. The 1,2-dithiolanyl rings must be involved in the initial step of the reaction sequence because they are the only constituents absorbing in the right spectral region [39]. Lipoic acid, for example, has a broad absorption band that extends from 280 to 410 nm ($\lambda_{\text{max}} = 333$ nm, $\varepsilon_{\text{max}} = 135$) [40]. The reduced solubilities of irradiated 1 and 2 may be explained by the photoinduced formation of intermolecular S-S bonds (photopolymerization), which is well known from lipoic acid [13]. The mutual orientation of the 1,2-dithiolanyl rings in the crystals of 1 and 2 (see Fig. 5) could favor such reactions.

Consequent reactions occur at the coordination centers. The infrared spectra unambiguously show that COO$^-$ groups have been transformed into COOH. The 1705-cm$^{-1}$ band and weak absorptions at 2500 - 2700 cm$^{-1}$, which develop during irradiation, are characteristic of carboxylic acids [41]. The aqua ligands are the most probable proton sources. This assumption is supported by the observation that the intensity of the original $\nu$(O-H) bands decreases on irradiation. The hydrogen-bonding networks (see Fig. 3) indicate that the proton transfer may proceed between adjacent coordination centers:

\[
2 \{(\text{COO})\text{M(OH)}_{2}\}^+ \rightarrow \{(\text{COOH})\text{M(OH)}_{2}\}^{2+} + \{(\text{COO})\text{M(OH)}\}
\]

At present we can only speculate about the final metal ion environment(s) in the irradiated products. So we must leave this question unresolved at this point.

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