

Synthesis, thermal behavior, and spectral properties of mixed-metal Cu(I)-VO(IV)-thiourea coordination polymers

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Abstract The heterometallic complexes $[\text{Cu}(\text{VO})_2(\text{CSN}_2\text{H}_4)_3\text{Cl}(\text{OH})_4] \cdot \text{H}_2\text{O}$, $[\text{Cu}_2(\text{VO})_2(\text{CSN}_2\text{H}_4)_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_4]$, and $[\text{Cu}_2(\text{VO})_3(\text{CSN}_2\text{H}_4)_4(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_4]$ were prepared and characterized in terms of their molecular electrical conductivity, electronic and IR spectra, and thermal behavior. A polymeric structure is proposed in which a thiourea ligand is bonded via a sulfur atom to the tetracoordinated copper(I) and via amino groups to the oxovanadium(IV) ion. The polymeric nature of the complexes is due to bridging via the OH, thiourea, and/or acetate moieties between oxovanadium(IV) coordination centers.

Keywords Copper · Vanadium · IR and VIS spectroscopy · Thermal behavior

Introduction

The chemistry of metal complexes containing sulfur donors as ligands has undergone spectacular development as these systems are genuine models for biological systems. These complexes also have practical use as corrosion inhibitors

[1] and precursors for new materials [2]. For example, metal sulfide thin films consisting of binary or ternary sulfides produced by the heating of different metal complexes of thiourea are very interesting from the point of view of industrial application [3]. The properties of these thin films depend on the nature and the composition of precursors, as well as on their methods of preparation and on their decomposition route [4–6]. For example, Naumov et al. [7] demonstrated the structural memory effect which means that each copper atom in the sulfide retains the coordination geometry it had in the complex. Recently, the preparation of semiconductor CuS nanosized particles by colloidal synthesis was reported. The stable colloidal dispersion of CuS nanoparticles was obtained by employing copper(II) acetate monohydrate as copper source and thiourea as sulfur source [8]. Covellite CuS with sub-microtubular structure was obtained by starting from copper(II)–thiourea complexes and the densification effect of vanadium on the covellite was underlined [9–11]. Starting from a copper(II)–thiourea system in a simple hydrothermal process, Cheng et al. obtained a ball-flower-shaped CuS structure and its efficiency as a photocatalyst was reported [12].

The thiourea molecule contains one sulfur and two nitrogen donor atoms and it can act as a tridentate ligand. It can also act as bridging [12] or non-bridging monodentate or bidentate ligand [13–15], resulting in a variety of structures. Depending on stoichiometry of the reactants and the preparative conditions, the composition and the nature of the product of the reaction between metal salts and thiourea can be very different.

In the literature more than 30 parent complexes of thiourea with different composition could be found, mostly with first row elements of transition metals. Studies of some 3d metal complexes with thiourea reveal monomer,

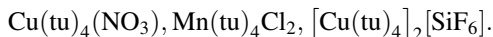
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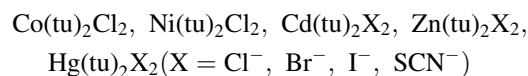
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dimer, tetramer, chain polymeric, and three-dimensional polymer structures [16–25] as follows (tu = CSN₂H₄):

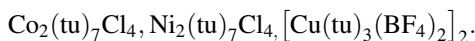
Monomeric structures with four sulfur atoms in tetrahedral arrangement around the metal ion [16–18]:



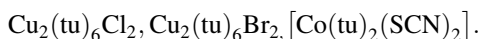
Monomeric structures with two sulfur atoms and two chloride anions in tetrahedral arrangement around the metal ion:



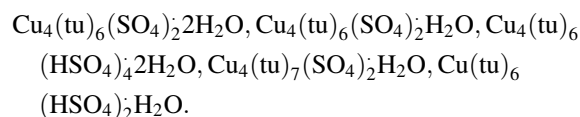
Dimeric structures with 4–4 sulfur atoms in a tetrahedral arrangement around the metal ion. In these structures, one of the ligand molecules acts as a bridging ligand via the sulfur atom and the other 3–3 ligand molecules act as a monodentate ligand via the sulfur atom [19–21]:



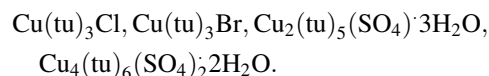
Dimeric structures with four sulfur atoms in a tetrahedral arrangement around the metal ion containing two thiourea molecules acting as monodentate ligands and two of them serving as bridging ligand between two metal ions [22]:



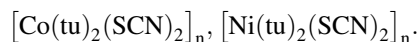
Tetranuclear structures with four trigonally coordinated metal ions with sulfur atoms of six ligand molecules (adamantane-type structure) [23–25]:



Chain-polymer structures with three sulfur atoms in trigonal planar arrangement or four sulfur atoms in tetrahedral arrangement around the metal ion; one of the ligands acts as a bridging ligand through the sulfur atom forming a polymer chain and each of the metal ions coordinates one or two other ligand molecules via a sulfur atom [22, 23]:



Two- or three-dimensional polymeric structures [21]:



Amongst the above mentioned compounds mainly Zn, Cu, Cd, and Sn complexes were investigated in some detail which is probably due to their potential industrial importance.

Besides the simple parent metal complexes of thiourea, the mixed-ligand complexes and the bimetallic complexes of thiourea are more interesting both for industrial uses and

for biological effects. Amongst bimetallic complexes, the copper and vanadium complexes of thiourea are interesting. Antimicrobial action of many copper [26, 27] or vanadium [28, 29] thiourea complexes has been reported [30]. Although many vanadium–copper heterometallic complexes are known [31–37], only a few papers report about heterometallic V–Cu–S complexes [38–43] and most of those complexes were obtained starting from reactants containing the thiovanadate moiety.

We report here the synthesis, spectral characterization, and thermal behavior of three heteronuclear copper–oxovanadium complexes containing thiourea as ligand.

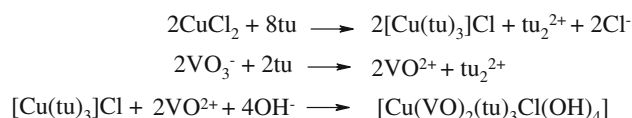
Results and discussion

The stereochemistry of the complexes containing thiourea as ligand depends strongly on many factors including metal to ligand ratio [44], nature of the counter ion, the solvent and, when the solvent is water, on the pH. Many of the copper complexes containing thiourea as ligand have been reported in the literature [45] (and references therein), their structures have been resolved by X-ray spectroscopy, and the reduction property of thiourea was proved. For instance, copper(I) complexes were obtained, although the starting material was a copper(II) salt and vanadium(V) was reduced to vanadium(IV). Under conditions described in the “*Experimental*” section, the reaction of NH₄VO₃, a copper(II) salt, and thiourea in aqueous media resulted in three new heteronuclear complexes with the formulae [Cu(VO)₂(CSN₂H₄)₃(Cl)(OH)₄]·H₂O (**1**), [Cu₂(VO)₂(CSN₂H₄)₂(C₂H₃O₂)₂(OH[−])₄]·2H₂O (**2**), and [Cu₂(VO)₃(CSN₂H₄)₄(C₂H₃O₂)₄(OH)₄] (**3**). On the basis of the studies by Doona and Stanbury [46], Scheme 1 is proposed for the synthesis of **1**.

The obtained complexes are microcrystalline solids, insoluble in water and in common polar organic solvents such as C₁–C₅ alcohols, acetone, acetonitrile, and chloroform, and slightly soluble in dimethylformamide and dimethylsulfoxide (DMSO). The low value of molar conductivities in DMSO shows that the complexes behave as non-electrolytes.

Visible spectra of the complexes

Inspection of the visible spectra of all the complexes shows the presence of two ligand-field transitions: one between



Scheme 1

830 and 865 nm and another near 460 nm. According to Ballhausen and Gray [47] the bands can be assigned to the $d_{xy} \rightarrow d_{yz}$, d_{xz} , and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, respectively, characteristic for the oxovanadium(IV) ion of C_{4v} symmetry.

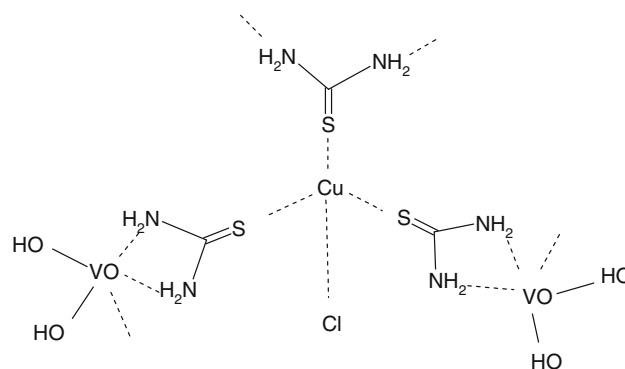
IR spectra of the complexes

The infrared spectra of the new compounds are very complex. However, bands assigned to the four sets of bands characteristic for the thioamide group can be identified. As a result of the complexation, some of these bands are shifted. Comparing the spectrum of free thiourea with that of all the complexes, we can make some general remarks. In the region 3,385–3,184 cm^{-1} bands assigned to the symmetric and antisymmetric $\nu(\text{NH}_2)$ modes as well as to $\nu(\text{OH})$ can be identified. These peaks are shifted to lower values in the spectra of the complexes. The very strong and sharp band at 1,614 cm^{-1} in the free ligand spectrum assigned to the $\delta(\text{NH}_2)$ mode appears as the largest one and is shifted to higher wavenumbers in the spectra of all the complexes. The breadth of this band denotes that the bending mode $\delta(\text{OH})$ is overlapped.

In the spectrum of the free ligand, the strong band in the region 1,465–1,409 cm^{-1} mostly originating from $\nu(\text{N}-\text{C}-\text{N})$, $\delta(\text{NH}_2)$, and $\nu(\text{C}=\text{S})$ modes is shifted toward lower wavenumbers and split for the metal complexes. The band of medium intensity in the free ligand at 730 cm^{-1} is attributed to $\nu(\text{N}-\text{C}-\text{N})$ and $\nu(\text{C}=\text{S})$. In the spectra of the complexes, this band appears as a doublet in the region 744–702 cm^{-1} . Also, the band at 628 cm^{-1} , which has an important contribution from $\nu(\text{CN})$, is split in the spectra of the complexes [48]. For all the complexes, a new sharp, well-defined peak appears in the region 819–875 cm^{-1} which is attributable to the OH bending mode [49]. The strong $\nu(\text{V}=\text{O})$ stretching band appears in the 934–963 cm^{-1} region in all complexes. The lower values for complexes **2** and **3** can be attributed to V–O–V association [50].

In accordance with the literature data, we assume that copper(I) is coordinated by the sulfur atoms of the ligand and of the oxovanadium by the nitrogen atoms of thiourea and oxygen atoms of the coordinated hydroxide group.

The spectra of complexes **2** and **3** are more complicated in the regions 1,590–1,630 and 1,500–1,400 cm^{-1} because of the presence of the acetate ligand. Most of the bands are covered by those of the thiourea ligands. However, the $\nu_a(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ modes can be identified at 1,518 cm^{-1} for both the complexes and at 1,478 for **2** and 1,498 cm^{-1} for **3**, respectively. The differences between the two frequencies, $\nu_a(\text{COO}^-) - \nu_s(\text{COO}^-)$, are of 40 and 20 cm^{-1} , respectively. According to Deacon and Phillips [51], it can be concluded that acetate ions act as bidentate



Scheme 2

chelating ligands. Additionally, for complex **3** a well-defined peak can be seen at 1,568 cm^{-1} which can be assigned to a $\nu_a(\text{COO}^-)$ mode of a bridging acetate [51].

On the basis of elemental analyses, molar conductivity values, and spectral properties, we propose a polymeric structure with a thiourea ligand bonded via a sulfur atom to the tetracoordinated copper(I) and via amino groups to the oxovanadium(IV) ion. The polymeric nature of the complexes is achieved by the OH bridges between oxovanadium(IV). The proposed structure of the molecular unit of complex **1**, illustrating the versatility of the thiourea ligand, is presented in Scheme 2. Here, thiourea can act as a bridging ligand between two oxovanadium(IV) ions belonging to the neighboring unit and as a tridentate ligand achieved by the two NH_2 groups making a four-membered chelate ring with the oxovanadium(IV) ion and the sulfur atom coordinating to the copper(I) center.

Thermal behavior of the complexes

The weight losses were followed by computer-controlled thermogravimetry (TG) analysis and by measuring the difference of masses of the sample before heating and masses of the cooled sample after the thermoanalytical experiments. A relatively large difference was observed between the masses of the sample heated to 800 °C (on TG curve) and the masses of sample cooled to room temperature after thermoanalytical measurements. This phenomenon is interpreted as a slow decomposition of the final product at 800 °C, which was followed in the course of the cooling period of the sample. A higher temperature of the heating process is not applicable, because at higher temperature (larger than 800 °C) the sulfur-containing decomposition products contaminate the sample holder or the metal parts of the instrument.

Two types of decomposition route were observed, and the thermoanalytical curves are shown in Figs. 1 and 2. In both cases the water content of the complexes left the solid matrices below 100–120 °C in endothermic processes, as is

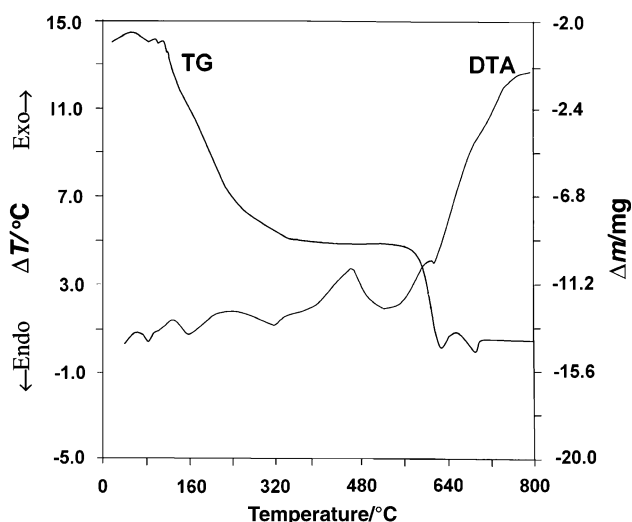


Fig. 1 Characteristic TG and differential thermal analysis (DTA) curves of complex **1**

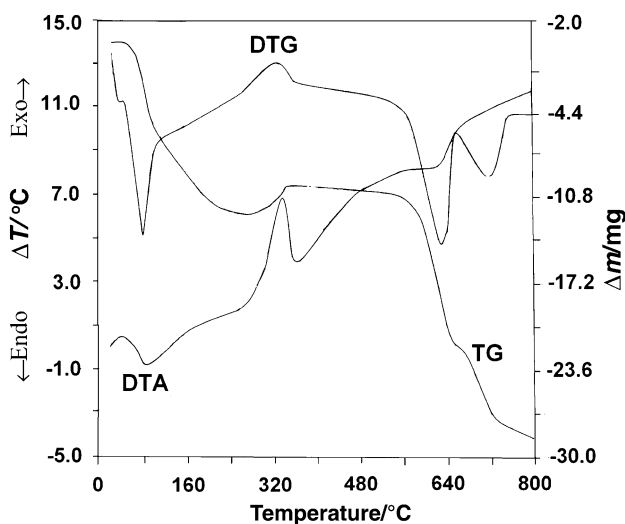


Fig. 2 Characteristic TG, derivative thermogravimetry (DTG), and DTA curves of complex **2**

to be expected generally. Above 120 °C, the complexes decompose in 3–4 exothermic or endothermic steps.

Complex **1** (Fig. 1) loses its water content below 120 °C in an endothermic reaction. At higher temperature, especially above 650 °C, the decomposition is followed by an exothermic heat effect, which can be assigned either to the starting of a new reaction in this temperature range or to the existence of an endothermic and exothermic process before 650 °C whose balance is an exothermic effect. On the TG curve four steps could be observed over the 120–190, 190–250, 250–370, and 500–700 °C temperature ranges.

The decomposition of complexes **2** and **3** (Fig. 2) is similar to that of complex **1**, with two differences: (1) the intensive decomposition starts at lower temperature (105 °C) and (2) in the temperature range between 270 and 360 °C a sharp peak was observed on the DTA curve, with increase of weight.

For interpretation of the thermal behavior of complexes, beside the TG and DTA curves, according to the cases noticed previously [52–56], the following data and considerations were used: in all cases the largest weight loss was observed over the 120–270 °C temperature range, where most of the organic part of the complexes left the solid phase and the thiourea molecules are destroyed. By the evolved gas analysis method, intermediate products of chemical reaction were observed (HCN, HSCN, CS₂, CO₂, H₂NCN, HCl, SO₂, NH₃, COS).

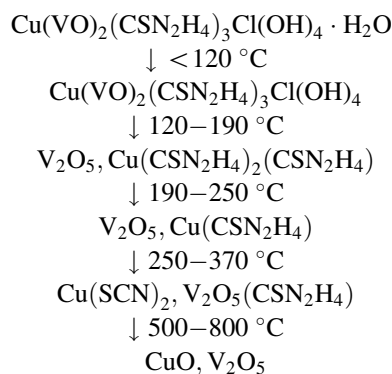
Different metal sulfur compounds, i.e., metal sulfate and metal thiocyanate, were found in the solid intermediate product. The final product was the oxide. In the course of the decomposition of thiourea, significant amounts of condensed organic phase (containing C, N, S atoms) were formed and left the solid phase at higher temperature. The intensive exothermic heat effect with little weight change of the sample at above 600 °C was assigned to the leaving of this organic phase.

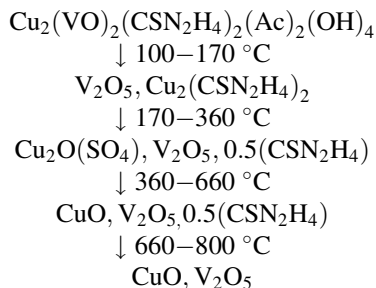
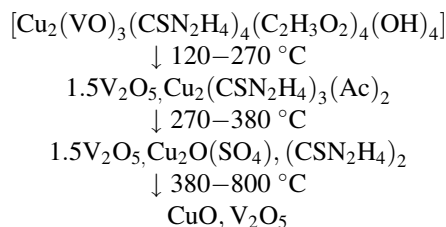
In both the copper and vanadium complexes the acetate moiety left the solid phase at low temperature (200–300 °C). The existence of VO(SO₄) and vanadium sulfides (VS₃, VS₂, V₂S₃) as intermediate products above 300 °C was excluded because of the formation of V₂O₅ at this temperature.

The formation of Cu₂O(SO₄) has been reported in the literature to occur at higher temperatures as an intermediate product when decomposition occurs in air. The final residual mass corresponded to the theoretical residue where CuO and V₂O₅ are formed.

On the basis of the above presented literature data, we propose the following decomposition schemes:

Decomposition scheme of complex **1**:



Decomposition scheme of complex **2**:Decomposition scheme of complex **3**:

Conclusions

Three new heterometallic complexes in the system Cu(I)-VO(IV)-thiourea were obtained. A polymeric structure is proposed in which the metal centers are connected through OH, thiourea, and acetate ligands. Also weak V–O–V interaction occurs. The thermal decompositions of the complexes are described and they support the spectral data. The decomposition of the complexes in air follows the same general scheme. However, the steps occur over different temperature ranges. Firstly, it can be noticed that all complexes are broken with the loss of counterions and formation of V₂O₅ and that the temperature of the first step is higher for **1** than for **2**, which can be correlated with the strength of V–O–V interaction as it results from $\nu(\text{V}=\text{O})$ values. Furthermore, complex **2** decomposes at a lower temperature which can be associated with the presence of the more labile chelated acetate ligand. IR spectra indicate the presence of two types of acetate ligands in **3**: a chelating one and a bridging type. Indeed, the thermal decomposition diagram of **3** shows that 2 mol of acetate is eliminated over the temperature range 120–270 °C whereas the next acetates are eliminated at higher temperature, denoting a more stable architecture created by the symmetrical, bridging acetate ligand. Further work is in progress in order to obtain crystals appropriate for X-ray analyses, which turned out to be difficult because of the polymeric character of the species.

Experimental

All reagents were used as purchased from Merck. Analytical data were obtained by a Perkin-Elmer Model 240C

elemental analyzer. Electrical conductivities were determined on an WTW LF-340 A conductivity meter. Electronic spectra were obtained on a UV/VIS Perkin Elmer Lambda 12 spectrometer on solutions and on Nujol mull. Infrared spectra of the solid complexes (KBr pellet) were recorded on an IR BIO-RAD FTS 135 spectrometer. The thermal analyses were performed over the 25–800 °C temperature range with a computer-controlled MOM derivatograph in air atmosphere, by using a ceramic crucible and $\alpha\text{-Al}_2\text{O}_3$ as a reference substance. The heating rate was 5 °C/min.

Synthesis of the complexes

Copper(I)di(oxovanadium(IV))chloridetetrahydroxotri-thiourea hydrate (Cu(VO)₂(CSN₂H₄)₃Cl(OH)₄·H₂O) (**1**, C₃H₁₈N₆S₃ClCuV₂O₇)

CuCl₂·2H₂O (0.42 g, 2.5 mmol), 0.29 g NH₄VO₃ (2.5 mmol), and 0.76 g thiourea (10 mmol) were dissolved in 12 cm³ water and the mixture was stirred and heated at 85 °C for 4 h. After cooling to room temperature, the olive green microcrystalline powder was separated by filtration, washed with cold water and ethanol, and dried over calcium chloride. Yield: 0.5 g (36%); IR (KBr): $\bar{\nu} = 3,368$ (m), 3,261 (m), 3,195 (m), 1,626 (s), 1,508 (w), 1,417 (m), 1,395 (w), 1,113 (m), 1,046 (w), 963 (s), 824 (m), 743 (w), 702 (m), 527 (m), 475 (w) cm⁻¹; UV–Vis (Nujol): $\lambda_{\text{max}} = 460, 730, 850$ nm; molar conductivity (DMSO): $\Lambda_{\text{m}} = 10.14 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

Dicopper(I)di(oxovanadium(IV))bisacetatotetrahydroxobisthiourea (Cu₂(VO)₂(CSN₂H₄)₂(C₂H₃O₂)₂(OH)₄) (**2**, C₆H₁₈N₄S₂Cu₂V₂O₁₀)

Cu(CH₃COO)₂·H₂O (0.49 g, 2.5 mmol), 0.29 g NH₄VO₃ (2.5 mmol), and 0.76 g thiourea (10 mmol) were dissolved in 12 cm³ water. The mixture was stirred and heated at 85 °C for 4 h and then cooled to room temperature. The dark green microcrystalline product obtained after filtration was washed with cold water and ethanol and dried over calcium chloride. The complex may contain small amounts of physically adsorbed water. Yield: 0.5 g (33%); IR (KBr): $\bar{\nu} = 3,380$ (m), 3,281 (m), 3,184 (m), 1,632 (s), 1,518 (m), 1,478 (m), 1,415 (s), 1,124 (m), 1,046 (w), 933 (s), 875 (s), 686 (m), 604 (s), 513 (s), 497 (m) cm⁻¹; UV–Vis (Nujol): $\lambda_{\text{max}} = 456, 780, 820$ nm; molar conductivity (DMSO): $\Lambda_{\text{m}} = 12.32 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$.

Dicopper(I)tris(oxovanadium(IV))tetraacetatotetrahydroxotetraphioureia (Cu₂VO)₃(CSN₂H₄)₄(C₂H₃O₂)₄(OH)₄) (**3**, C₁₂H₃₂N₈S₄Cu₂V₃O₁₅)

Compound **3** was prepared similarly to compound **2**, except for the amount of thiourea, which was 1.90 g (2.5 mmol). The complex may contain small amounts of physically adsorbed water. Yield: 0.59 g (25%) of olive green

microcrystalline powder; IR (KBr): $\bar{\nu} = 3,385$ (m), 3,297 (m), 3,187 (m), 1,624 (s), 1,568 (m), 1,519 (m), 1,498 (m), 1,407 (s), 1,395 (w), 1,098 (w), 942 (m), 819 (m), 744 (w), 701 (m), 603 (w), 587 (m), 472 (w) cm^{-1} ; UV–Vis (Nujol): $\lambda_{\text{max}} = 460, 865$ nm; molar conductivity (DMSO): $\Lambda_{\text{m}} = 7.45 \text{ } \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$.

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