energetically favored conformation of all the ethyl conformers observed in the crystals.

Another important result of the Raman investigation is that π–π aggregation in the triclinic B crystals of both Cu- and NiOEP results in structural changes similar to those occurring upon aggregation in solution. This similarity is observed in spite of probable differences in substituent orientations in the solution and crystal cases. This result indicates that it is the π–π interactions that are important in determining the monomer–aggregate

structural differences, not the substituent orientations.

Luminescence of Copper(I) Arenethiolates and Its Relation to Copper(I) Luminescence in Other Complexes

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The luminescence properties of some trinuclear copper(I) arenethiolates are reported and discussed. Two of these copper(I) arenethiolates, i.e., $[CuSC_6H_4[(R)\text{-}CH(Me)NMe_2]\text{-}2]_3$ and $[Cu_3\{SC_6H_4[(R)\text{-}CH(Me)NMe_2]\text{-}2\}_2(C\equiv\equiv Ct\text{-}Bu)]_2$, show triboluminescence. The optical transitions in these copper(I) compounds are assigned to ligand-to-metal charge transfer (LMCT). It is proposed that the formation of a three-electron two-center sulfur–sulfur bond in the excited state lowers the excitation energy of these trinuclear copper(I) arenethiolates. Structural information about lone pair orientation in copper(I) arenethiolates can be derived from UV/vis data as is shown for $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$. A comparison with optical transitions on Cu(I) complexes reported in the literature is also made.

Introduction

It is well known that certain Cu(I) complexes show efficient luminescence.[2,3] The nature of the transition involved has been interpreted in different ways. On the one hand, the transition has been ascribed to a metal-to-ligand-charge transfer (MLCT) where an electron is transferred from the copper(I) center to the unoccupied π* orbital of the ligand.[3] On the other hand, the occurrence of a metal-centered transition is also possible. In this case an electron is promoted from the 3d level to the 4s or 4p level.[4]

Recently we reported the synthesis and structural characterization of a novel class of copper(I) arenethiolates, $[CuSC_6H_4\text{-}[(R)\text{-}CH(Me)NMe_2]\text{-}2]_3$ (1; $[CuSAr']_3$) and $[CuSC_6H_4\text{-}(CH_2NMe_2)\text{-}2]_3$ (2; $[CuSAr]_3$).[5] These compounds have a trinuclear structure, and 1 has been structurally characterized (shown in Figure 1a) by a single-crystal X-ray structure determination. Particular interesting features of these compounds are the chair-like conformation of the six-membered Cu_3S_3 ring, the equatorial binding of the aryl groups to the Cu_3S_3 ring, and the intramolecular coordination of each of the *ortho*-CH(Me)NMe$_2$ substituents to a copper atom, resulting in a trigonal coordination geometry of each of these atoms (see Figure 2a). Strong evidence for a second possible structure for these compounds has been obtained from NMR studies in which one of the three aryl groups is axially bonded to the Cu_3S_3 ring (see Figure 2b).

Replacement of one of the arenethiolate groups by an alkynyl group $(C\equiv\equiv Ct\text{-}Bu)$ resulted in the synthesis of a further class of novel copper(I) arenethiolates, $[Cu_3(SAr')_2(C\equiv\equiv Ct\text{-}Bu)]_2$ (3) and $[Cu_3(SAr)_2(C\equiv\equiv Ct\text{-}Bu)]_2$ (4), which have the hexanuclear

structure shown in Figure 1, parts b and c, respectively.[6] These structures are brought about by dimerization of two trinuclear units [compare the schematic structures of $[CuSAr]_3$, a and b, with the $Cu_3(SAr)_2(C\equiv\equiv Ct\text{-}Bu)$ units, c and d, of $[Cu_3(SAr)_2\text{-}(C\equiv\equiv Ct\text{-}Bu)]_2$ in Figure 2]. These monomeric units consist of a six-membered Cu_3S_2C ring in the boat conformation, with the aryl groups bonded either one equatorially and one axially (Figure 2d) or exclusively axially (Figure 2c) to the Cu_3S_2C ring.

A remarkable feature of these compounds is that the chiral compounds **1** and **3** show an intense triboluminescence which is visible even at broad daylight. Upon mechanical disruption the crystals emit light. This prompted us to study the photoluminescence properties of this type of compounds in more detail. We have studied the latter, because the triboluminescence is difficult to measure and the triboluminescence spectra are usually comparable to the photoluminescence spectra.[7,8] This was by visual inspection also the case for the present compounds.

Experimental Section

Materials. The syntheses of $[CuSC_6H_4[(R)\text{-}CH(Me)NMe_2]\text{-}2]_3$ (1), $[CuSC_6H_4(CH_2NMe_2)\text{-}2]_3$ (2), $[Cu_3\{SC_6H_4[CH(Me)NMe_2]\text{-}2\}_2(C\equiv\equiv Ct\text{-}Bu)]_2$ (3), and $[Cu_3\{SC_6H_4(CH_2NMe_2)\text{-}2\}_2(C\equiv\equiv Ct\text{-}Bu)]_2$ (4) have been described elsewhere.[5,6]

Photoluminescence. Excitation and emission spectra were recorded on a Perkin-Elmer MPF 44B spectrofluorometer equipped with an Oxford Instruments CF204 liquid He cryostat. Suitable filter sets were chosen for selecting the signals. Emission spectra were corrected for photomultiplier sensitivity, and excitation spectra were corrected for the intensity of the excitation source and transmission of the monochromator. The decay times were measured using a pulsed N_2 laser (Molectron UV 14) as an excitation source. The luminescence was focused onto the entrance slit of a Spex 1704X 1-m monochromator and detected with a cooled RCA C 31034 photomultiplier. The signal was processed with a ORTEC photon-counting system.[9]

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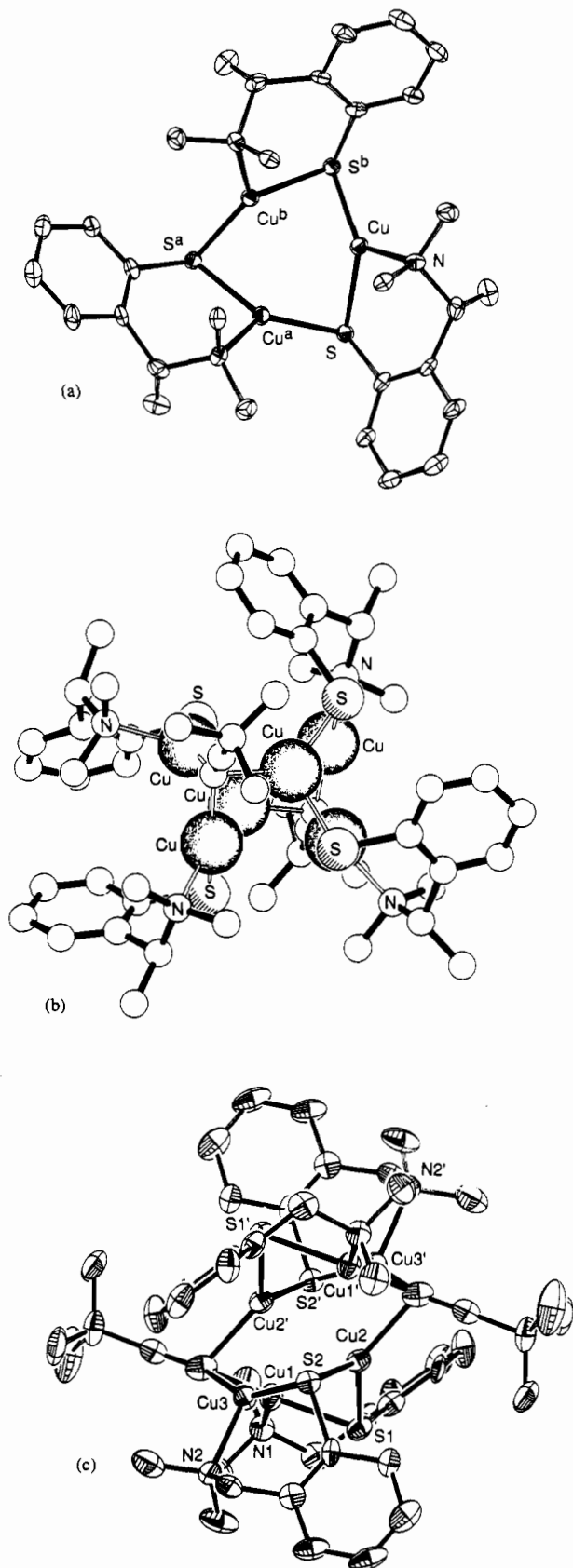(9) van Vliet, J. P. M.; Blasse, G.; Brixner, L. H. *J. Electrochem. Soc.* **1988**, *135*, 1574.

Figure 1. Structures in the solid state of (a) [CuSC$_6$H$_4$[(R)-CH(Me)-NMe$_2$]-2] (**1**); (b) [Cu$_3${SC$_6$H$_4$((S)-CH(Me)NMe$_2$)-2}$_2$(C≡Ct-Bu)]$_2$ (**3**); and (c) [Cu$_3${SC$_6$H$_4$(CH$_2$NMe$_2$)-2}$_2$(C≡Ct-Bu)]$_2$ (**4**).

Results

The compounds [CuSC$_6$H$_4$[(R)-CH(Me)NMe$_2$]-2] (**1**; [CuSAr′]$_3$) and [CuSC$_6$H$_4$(CH$_2$NMe$_2$)-2] (**2**; [CuSAr]$_3$) appear as yellow and white solids, respectively. [Cu$_3$(SAr′)$_2$(C≡Ct-Bu)]$_2$ (**3**) and [Cu$_3$(SAr)$_2$(C≡Ct-Bu)]$_2$ (**4**) are both yellow colored. We

did not find a significant dependence of the luminescence properties of these compounds on their preparation history. They are stable on irradiation with UV light and for exposure to air for at least 1 day. Compound **1** crystallizes from a concentrated tetrahydrofuran solution as large yellow crystals of the THF solvate: **1**·THF. So far, we have only isolated **2** and the racemic mixture of **1** as amorphous materials which were not found to have any triboluminescence properties. Compounds **3** and **4** were crystallized from a concentrated dichloromethane solution.[6] Only **1** and **3** emitted light when they were mechanically disrupted, although the basic structures of the complexes **3** and **4** are very similar.

The luminescence spectra at 4.2 K of both **1**·THF and **1** show an excitation maximum at 400 nm and an emission maximum at 555 nm (Figure 3), so that the Stokes shift is about 7500 cm^{-1}. The emission spectrum of **1** consists of a broad band without fine structure. At higher temperatures the emission band broadens, but the integrated area remains constant. The bandwidth at half-height [= $\delta(T)$] of this emission band at T K is $\delta(300$ K$)$ = 3800 cm^{-1} and $\delta(10$ K$)$ = 2100 cm^{-1}. The temperature dependence of $\delta(T)$ yields, using eq 1, a value for the vibrational frequency involved, ν_e, of some 150 cm^{-1}.[10] In eq 1 the parameter

$$\delta(T) = \delta(0)\left[\tanh\frac{h\nu_e}{2kT}\right]^{-1/2} \quad (1)$$

δ represents the half-width of the emission band, and the other symbols have their usual meaning.

The decay curves were exponential. The temperature dependence of the decay times shows that the radiative processes involved have to be described with at least a three-level system (see Figure 4). At low temperatures, the decay time, τ, is 350 μs and at room temperature, 6.0 μs. Between these extremes, a weighted average decay time τ is observed. By using eq 2, a satisfying fit can be

$$\frac{1}{\tau} = \frac{1}{\tau_0}\frac{e^{(\Delta E/kT)}}{1 + e^{(\Delta E/kT)}} + \frac{1}{\tau_1}\frac{1}{1 + e^{(\Delta E/kT)}} \quad (2)$$

found which matches the experimentally found τ values with ΔE = 14.5 cm^{-1} ($\pm$1.5), where ΔE represents the energy difference between the two excited states, τ_1 = (6 $\pm$ 2) μs, and τ_2 = (350 $\pm$ 20) μs.[11] It must be noted that eq 2 is only valid under the assumption that the nonradiative transitions between the two excited levels proceed at a higher rate than the radiative transitions. Furthermore, τ_0 and τ_1 are assumed to be temperature independent.

The excitation spectrum of the emission of **2** shows two excitation maxima, viz., 350 and 400 nm (see Figure 3). When the excitation spectrum is measured for 480-nm emission, only the excitation band at 350 nm is observed. The 400-nm excitation band is accompanied by the 350-nm excitation band when the excitation spectrum is measured for 610 nm. The 480-nm emission band is accompanied by the 610-nm emission band when the emission spectrum is recorded for 290-nm excitation (the 350-nm excitation band). However, when irradiating into the 400-nm band (with 440 nm), only the 610-nm band can be observed separately in the emission spectrum. Consequently, the 350-nm excitation band is connected to the 480-nm emission band which points to a Stokes shift of about 8500 cm^{-1}. The 400-nm excitation band corresponds to the 610-nm emission band with a Stokes shift of about 9000 cm^{-1}. Figure 5 shows the integrated area of the emission bands, for both the 480- and 610-nm emitting centers, as a function of temperature upon excitation with UV light of 290 nm. At room temperature both centers are quenched, whereas excitation with light of 440 nm shows that the integrated area of the 610-nm emission band remains constant up to room temperature. A slight broadening of the 610-nm band is observed; $\delta(255$ K$)$ = 3400 cm^{-1}, $\delta(10$ K$)$ = 3200 cm^{-1}.

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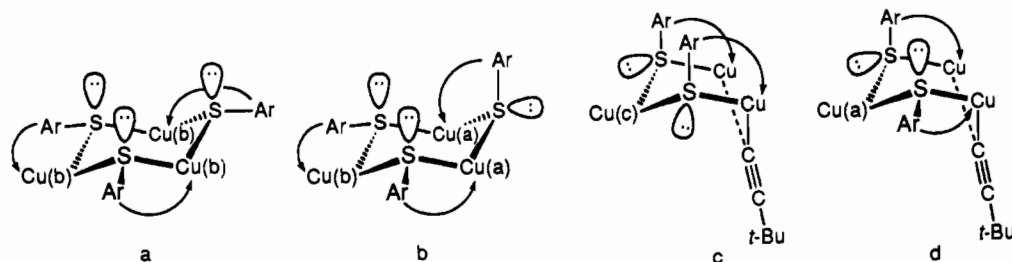(11) DiBartolo, B. *Optical Interaction on Solids*; Wiley: New York, 1968.

Figure 2. Schematic structures of trinuclear copper units: (a) **1**; (b) **2**; (c) one of the two $Cu_3(SAr)_2(C\equiv Ct\text{-Bu})$ units of **3**; and (d) the Cu_3-$(SAr)_2(C\equiv Ct\text{-Bu})$ unit of **3** and **4**.
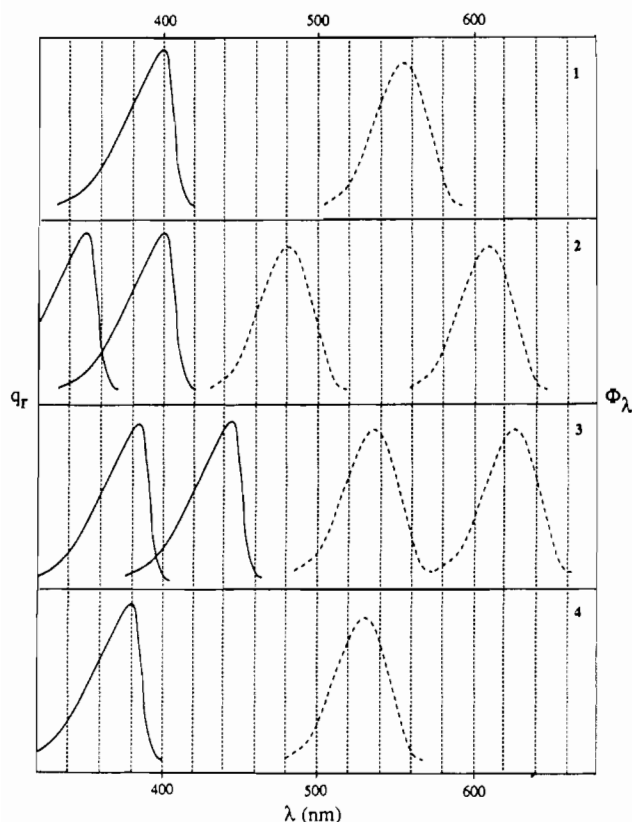

Figure 3. Excitation (—) and emission (---) spectra of the luminescence of **1–4** at liquid helium temperature. q_r denotes the relative quantum output and Φ_λ the spectral radiant power per constant wavelength interval, both in arbitrary units.
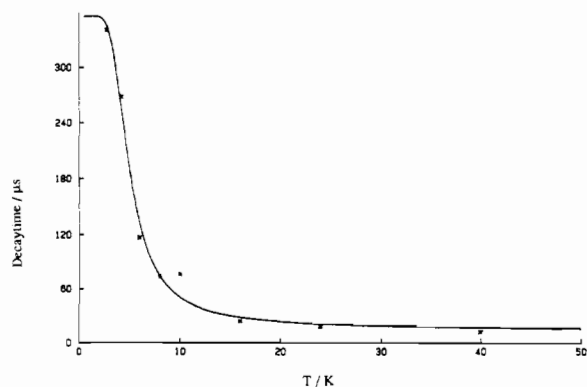

Figure 4. Decay times of the luminescence of **1** as a function of temperature. λ_{ex} = 337 nm. The full line represents the best fit of the data to eq 1. In the temperature range 2–40 K, the luminescence intensity is temperature independent (see also text).

The luminescence spectra of **4** show (see Figure 3) one excitation maximum at 380 nm and a corresponding emission maximum at 530 nm (Stokes shift 8000 cm⁻¹). The bandwidth at half-height [= $\delta(T)$] of the emission band was temperature dependent: δ(4.2 K) = 1820 cm⁻¹ and δ(170 K) = 2315 cm⁻¹, which
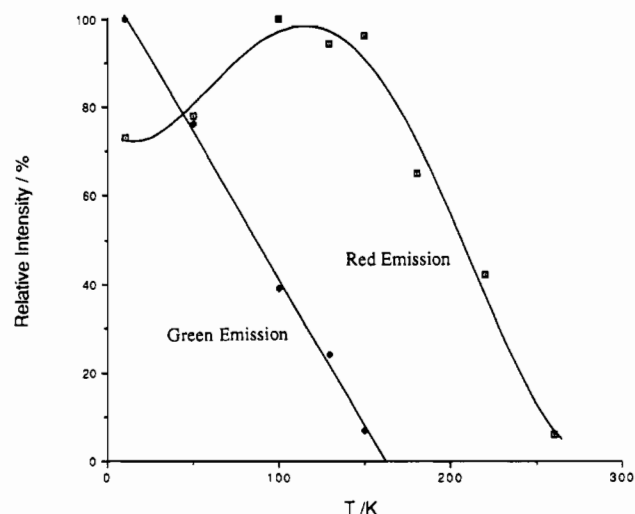

Figure 5. Integrated intensity of the green emission band and red emission band of **2** as a function of temperature upon irradiation with 290 nm. The scale is relative to the maximum intensity (100%).

yields again an effective vibrational frequency of about 150 cm⁻¹. The intensity of the emission band is constant from 4 to 170 K. At temperatures above 170 K, the intensity decreases with a minimum at around 260 K, whereafter the intensity increases.

The luminescence spectra of **3** have each two maxima like in the case of **2** (see Figure 3). One excitation maximum at 385 nm with an emission band at 525 nm, and one excitation maximum at 445 nm with an emission band at 650 nm. The Stokes shifts are 7500 and 8000 cm⁻¹, respectively. When the intensity was measured as a function of temperature, the intensity of both emission bands shows, just as in the case of **4**, a minimum (40% of the maximum intensity) at 140 K. The bandwidth at half-height of the emission band at 650 nm is temperature independent, while the other emission band, at 525 nm, shows a broadening when increasing the temperature; δ(5 K) = 1730 cm⁻¹ and δ(212 K) = 2470 cm⁻¹, yielding roughly the same vibrational frequency ($\sim$150 cm⁻¹).

Discussion

Photoluminescence of the CuSAr Complexes. The spectra of **1** show one emission and one excitation band, and the Stokes shift amounts to 7500 cm⁻¹. This compares favorably with, for example, the Stokes shift observed for $[Cu(PPh_2CH_3)_2dmp]^+$.[3] Analysis of the decay times points to the presence of two excited levels. The one at lower energy has a longer radiative decay time than the upper one, which results from the triplet and singlet character of these energy levels, respectively.[3] The energy difference between the two is rather small (14.5 cm⁻¹): an assignment to zero-field splitting cannot be excluded.

The luminescence of **2** is more complicated. The spectra of **2** clearly show two different emission bands with maxima at about 480 and 610 nm (hereafter indicated as the green and the red band, respectively). The red band has a Stokes shift of 9000 cm⁻¹ and an own excitation band. Up to 300 K no thermal quenching is observed. These properties are similar to those observed for **1**. In contrast to the red emission, the green emission cannot be excited solely. Its excitation maximum is at about 350 nm,
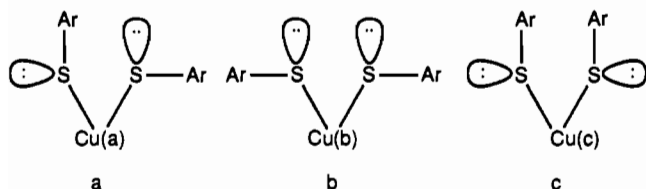
Figure 6. Relative orientation of the aryl group (Ar) and the lone-pair electrons on sulfur of the neighboring SAr groups as found in **1–4**: (a) in **2–4**; (b) in **1** and **2**; (c) **3**. They have been ordered with respect to increasing excitation energies observed in the present experiments.
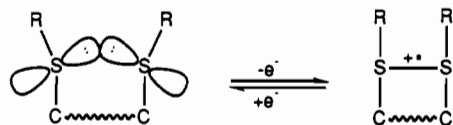

Figure 7. Reduction of a disulfide; the p-type lone pair electrons of the sulfur atoms form a three-electron sulfur–sulfur bond. Note: the hybrid orbital type lone pair on both sulfur atoms is left out.

suggesting a Stokes shift of 8500 cm^{-1}. When irradiation is into the green excitation band, the red emission band is also observed.

The temperature dependence of the red and green emission intensities upon excitation at 290 nm is remarkable (Figure 5). The green emission is quenched at about 150 K. The red emission intensity increases in the quenching range of the green band, i.e., the green excitation energy is transferred to the red-emitting center. Furthermore, the excitation band at 400 nm cannot be observed separately, while the band at 350 nm can. This also indicates that the excitation energy of 350 nm used to excite the green-emitting center is transferred at least partly to the red-emitting center. This is in agreement with the spectral data (Figure 3b): the excitation spectrum of the red-emitting center contains the excitation band of the green-emitting center. These observations exclude the possibility that the two emissions originate from different molecules.

On the basis of the above, we can assign the two emissions to the different copper(I) centers in **2**. Figure 2b shows that Cu(b) is coordinated to two sulfur atoms which have their electron lone pairs oriented parallel to each other and perpendicularly with respect to the plane through the three sulfur atoms of the [CuSAr]$_3$ complex (Figure 6b). However, the Cu(a) atoms are coordinated to sulfur atoms which have their electron lone pairs oriented perpendicularly to each other (Figure 6a). In **1** all copper atoms are equivalent and comparable to Cu(b) in **2**. Therefore, we assign the red emission to a copper center with a coordination around the copper atom similar to Cu(b). The copper centers in **1** as well as the Cu(b) center in **2** have the same position of their excitation band, viz. ~400 nm. The green band can then be ascribed to Cu(a), which has its excitation band at higher energy. From NMR observations,[12] and the results of the photoluminescence measurements, we conclude that **2** exists as the C$_1$ conformer (Figure 2b) in the solid state.

Although the spectra of **3** and **4** are different (see Figure 3), there are still some similarities. In both cases there is a minimum in the intensity of the emission band as a function of temperature, and both have an excitation band at 385 nm with a corresponding emission band at 530 nm. The decrease and later increase of the emission intensity as a function of temperature is not understood. On the basis of the temperature dependence of the half-width of the 530 nm emission band, both complexes have an effective vibration frequency of about 150 cm^{-1}. Because of this similarity, the emission band at 530 nm can be ascribed to the presence of the identical unit (see Figure 2d) in both complexes. The difference between the complexes **3** and **4** is the emission band at 650 nm (excitation 445 nm) in **3**. This band can be ascribed to the Cu$_3$ unit which has both its aromatic groups axially bonded to the Cu$_3$S$_2$C ring (see Figure 2c).

The orientation of the lone pairs and aryl groups on neighboring sulfur atoms to the copper in **4** are similar to that of Cu(a) in **2** (Figure 6a). Indeed, the excitation and emission maxima of **4**

are at about the same energy as the green band in **2**. In **3** there are two separated luminescence systems, one of which is identical to that of **4**. This system is similar to the Cu(a) center in **3** (Figure 2d). The other system (Figure 2c) with Cu(c) has the aryl groups parallel in an axial position to the Cu$_3$S$_2$C ring (Figure 6c). Because of the lower excitation energy needed to excite the Cu(c) system, the excited state must be more delocalized than in other systems such as Cu(b). The reason for this lower excitation energy and higher degree of delocalization is that in the Cu(c) excitation system (i) the participating orbitals have the right symmetry [compare Cu(a)] and (ii) the overlap of the lone pair electrons on the sulfur is larger than in the case of Cu(b).

In order to describe the nature of the optical transitions on these copper complexes, we consider organosulfides and, in particular, organodisulfides (i.e., dithioethers and dithiols) which are known to be good reductors.[13] The one-electron oxidation of organosulfides has been extensively studied.[13–15] These radical cations are known to be stable, and oxidation to the corresponding dications occurs with remarkable ease. These oxidations are done chemically or electrochemically. Organo sulfur atoms have two different lone pair electrons. One is of the p-orbital type which is perpendicular to the C–S–C plane, and the second is a hybrid orbital (sp^2) which has a lower electron density than the first type.[16] If the former orbitals point to each other, the redox potential of the disulfide will be lower compared to that for a parallel orientation.[14] The stability of the cationic disulfide is due to the well-established sulfur–sulfur bond formation.[15] This is a two-center three-electron bond ($\sigma^2\sigma^{*1}$) with the radical electron in the antibonding σ orbital (Figure 7). These oxidations of organic disulfides are known to be reversible as well as the nitrogen analogons.[17]

These findings suggest that the optical transitions on the present copper complexes are of the LMCT type, since sulfur preferentially acts as a reducing ligand. Depending on the stabilization of the hole on the sulfur atoms, the excitation energy for the different copper centers, surrounded by two sulfur atoms (Figure 6), increases in the same way as the redox potential of the organodisulfide does with respect to the orientation of the sulfur lone pair electrons.

In compound **2**, quenching of the green emission in favor of the red emission (Figure 5) is ascribed to energy transfer from the green-emitting center to the red-emitting center. The necessary spectral overlap is clearly visible in Figure 3. At 4.2 K the green excitation band (extending down to 460 nm) shows spectral overlap with the red excitation band (extending up to 400 nm); at higher temperatures this spectral overlap increases rapidly since the

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(12) In solution, NMR results of **1** and **2** indicate the existence of two isomers.[5] These NMR results indicate that, in solution, **1** and **2** exist in two configurations, C$_3$ and C$_1$, which are in equilibrium via inversion of the sulfur configuration (see Figure 2a,b). The C$_3$/C$_1$ ratio in compound **2** is 1:9, which, however, does not necessarily have to be the ratio in the solid state. A molecular reorientation at such low temperatures in the solid state is unlikely. If **2** were to occur as a C$_3$ conformer in the solid state, then **2** would have properties similar to those of **1**. Compound **1** exists as a 3:2 C$_3$/C$_1$ isomer mixture in solution but crystallizes completely as the C$_3$ conformer in the solid state.

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Table I. Literature Survey of the Absorption and Emission Maxima of Cu(I) Complexes[a]

species[b]	max absorption band	max emission band	ref
CuCl$_3^{2-}$ (aq)	37	21	18
Cu(I) in SiO$_2$ glass	38.5	20	19
LiSrPO$_4$:Cu(I) (s)	~37	24	20
Cu(I) in phosphate glass	37	23	21
Cu(I) in SiO$_2$ glass	37	23	20
NaCl:Cu(I) (s)	36	29	22
Cu(I) monomer in β''-alumina		23	23
Sr$_3$(PO$_4$)$_2$:Cu (s)	~33	22	24
Cu(a), compound 2 (m)	28.5	20.5	this work
Cu$_4$I$_4$(py)$_4$	28	14	40
CuI-pyridine	27	17	25
Cu(a), compound 4 (m)	26	18	this work
Cu(a), compound 3 (m)	26	18.5	this work
Cu(I) pairs in β''-alumina		19	23
[Cu{P(Ph)$_2$(CH$_3$)}{dmp}]$^+$ (m)	26	19	3
[Cu(PPh$_3$)$_2$(phen)]$^+$ (m)	25	18.5	3
CuLaO$_2$ (s)	25	18	26
Cu(b), compound 2 (m)	25	16	this work
Cu(b), compound 1 (m)	25	17.5	this work
Cu(c), compound 3 (m)	22.5	14.5	this work
Cu(phen)$_2^+$ (aq)	21	14	27
Cu$_2$O (s)	17.5		28
Cu$_2$WO$_4$ (s)	~17		29
CuNbO$_3$ (s)	~17		30
CuInS$_2$ (s)	~12		31
Cu$_2$S (s)	10		32
Ag(I) tetrameric complexes	35	20	33

[a] All values in 10^3 cm^{-1}. [b] s, solid; m, molecular; aq, in water solution.

spectral bands involved become broader. Whether a certain amount of transfer occurs already at 4.2 K is hard to say, since the radiation used to excite Cu(a) excites also Cu(b). The broadening of the emission bands is due to the low frequency of the vibration involved (~150 cm^{-1}), and this effect is already considerable at 100 K. The vibration involved is probably due to some bending mode of the (CuSAr)$_3$ complex.

The observation that the red emission is quenched below room temperature for excitation with 290 nm can be due to the fact that the green emission is quenched, so that the nonradiative rate in the green-emitting center competes successfully with the transfer rate. The effect cannot be intrinsic, since direct excitation in the red excitation band does not show this quenching. It can be excluded that photochemical decomposition occurs for the shorter wavelength excitation, since the compound does not decompose under UV radiation.

In the next paragraph we will compare the nature of these optical transitions with data on the luminescence of Cu(I) reported in the literature.

Comparison with Other Cu(I) Emissions. Table I shows a survey

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of the maxima of the emission and absorption (excitation) bands of a selection of Cu(I) species. The position of the last five copper compounds in this table is rather inaccurate, since they show only broad absorption bands. We have also added an example of an Ag(I) luminescence. The spectra of the compounds listed show a pronounced shift from 38 000 to 10 000 cm^{-1}. The Stokes shift of the emission is $(9 \pm 2) \times 10^3$ cm^{-1}, except for the less well-defined species CuCl$_3^{2-}$ in solution, Cu(I) in glass, Cu(I) in LiSrPO$_4$, and the tetranuclear Cu$_4$I$_4$(py)$_4$ cluster where it is larger.

The literature gives different assignments for the optical transitions involved; one is that the transitions are of the type 3d^{10} → 3d^{9}4s and 3d^{9}4p on the Cu(I);[4] another is that the transitions are of the MLCT type;[3] there are also authors who ascribe the shift to lower energy to Cu(I) pair formation assuming overlap of the Cu(I) wave functions.[23,24] For the sulfur ligands ligand-to-metal charge transfer (LMCT) is very probable (see above). This interpretation has also been used by Ford et al.[40] (iodide-to-copper CT). Nevertheless, Table I suggests that there is one transition involved, the spectral position of which shifts to lower energy with increasing covalency.

In ionic compounds the absorption transition will mainly be 3d^{10} → 3d^{9}4s and 3d^{9}4p. However, if the ligands have empty orbitals of the correct symmetry and energy available, these will mix with the s and p orbitals of copper(I), and as a consequence the absorption transition moves to lower energy and obtains MLCT character. Actually, Ford et al.[40] describe the emission transition in Cu$_4$I$_4$(py)$_4$ as a mixture of LMCT and a Cu(I) centered transition. If there are more ligands, and/or if the copper complexes form bigger aggregates, there will be more delocalization and the absorption transition will move further to lower energy. The ionic 3d^{10} → 3d^{9}4s interpretation has very recently been criticized by Van Tol.[39] He was unable to detect the 4s electron by ESR techniques in a NaF:Cu(I) crystal. In order to explain this, he suggests also some type of (undefined) electron transfer.

These facts suggest that a more general description of the transitions under discussion should be given. Following McGlynn et al., we can approach this as follows.[34] Consider the simple system Cu$^+$L$^-$. The ground configuration is written $\Psi_G = \Psi(Cu^+L^-)$. There are several excited configurations, viz., $(Cu^+)^*L^-$ (Ψ_1) (excitation on copper), CuL (Ψ_2) (LMCT), and Cu^{2+}L^{2-} (Ψ_3) (MLCT). The excited state can be written as eq 3. It is

$$\Psi_E = a\Psi_1 + b\Psi_2 + c\Psi_3 \tag{3}$$

clear that this can be extended with terms like $\Psi_4[Cu^+(L^-)^*]$ and $\Psi_5[CuCu^{2+}]$ (copper–copper interaction). The position of the spectral transition depends on the values of a, b, c, etc.[34] On top of Table I, the value of a is much larger than that of the others. In the case of the sulfide ligands the value of b might be larger, and for other ligands c might dominate. Quantitative calculations which will necessarily be of a complicated nature are required to specify the optical transition any further. We conclude that the literature approaches these transitions in a too simple way by using only one configuration in the excited state.

The CuSAr complexes fit in this table. The Cu(a) atoms in [CuSC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_3$ (2) and Cu(a) in [Cu$_3${SC$_6$H$_4$[(R)-CH(Me)NMe$_2$]-2}$_2$(C≡Ct-Bu)]$_2$ (3) and [Cu$_3${SC$_6$H$_4$-(CH$_2$NMe$_2$)-2}$_2$(C≡Ct-Bu)]$_2$ (4) have their absorption transition at a relatively high energy. This suggests that the sulfur atoms which are bonded to one copper, and have their lone pairs per-

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pendicular, have a some what lower ground state and/or higher excited state. On the other hand, the excited state of Cu(c) with two neighboring sulfur atoms, which have their aryl groups parallel, is lower (and/or the ground state is higher) because the electron repulsion is changed into an attracting three-electron sulfur–sulfur bond (see Figure 7). At low temperatures, the excited state in **2** on Cu(b) remains on one side of the complex, whereas the one on Cu(a) stays at the other. At higher temperatures energy transfer occurs which results in localization of the excited state at Cu(b), from where emission occurs.

In $[CuSC_6H_4[(R)-CH(Me)NMe_2]-2]_3$ (**1**), the copper atoms are all identical and of the Cu(b) type. The broadness of the spectral bands and the considerable Stokes shift indicates that electron-vibrational coupling is strong. This suggests that the excited state remains localized due to relaxation. The Stokes shift

in **2** (9000 cm^{-1}) is somewhat larger than in **1** (7500 cm^{-1}). This might be explained by a delocalization of the hole in excited **1** via the lone electron pair orbital of the third sulfur which has the right symmetry to form a five-electron three sulfur center bond. This, in turn, results in a less outspoken relaxation around the central copper atom, so that the Stokes shift is also less.

From this we conclude that the excited state is not delocalized over the Cu_3 unit or the aromatic rings. Murphy et al. have recently reported room temperature luminescence from tetrametallic complexes of ruthenium.[35] They ascribed this to localization of the MLCT transition involved. This runs parallel to our view. The competition between localization and delocalization has been discussed by one of us elsewhere.[36] Other examples are localization of the chromate tetrahedra[37] and the localization in the different molybdate groups in $MgMoO_4$.[38]
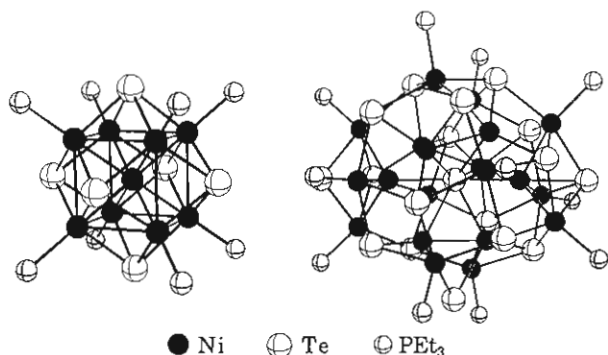

Relationships between Extended Structures and Molecular Clusters of Nickel and Tellurium

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The synthesis of bulk NiTe from molecular precursors of the zero-valent elements under very mild conditions was previously reported. In that study, two molecular intermediate clusters, $Ni_9Te_6(PEt_3)_8$ and $Ni_{20}Te_{18}(PEt_3)_{12}$ were also isolated. Consequently, the idea of structurally relating the molecules to the solid emerged. In this work we relate a cut, extracted from the solid NiTe, to each of the two clusters. The structural relation of the smaller cluster to the bulk is very clear; extended Hückel calculations actually favor a geometry between the observed cluster structure and hypothetical cut from the solid. The bigger cluster, although apparently complex and intricate, is also derivable from the bulk, if one includes two interstitial Ni atoms, as found in a related Ni_2In structure.

The preparation of extended atomic arrays in the solid state from molecular precursors has been much developed within the last decade. This approach allows higher reaction rates and hence lower temperatures than the classic ceramic preparative routes. In this context, Steigerwald and co-workers[1] were seeking an advantageous technique to prepare large intermetallic clusters. They decided to synthesize the solid-state compound nickel telluride, NiTe, using organometallic complexes of zero-valent tellurium and nickel, in particular, bis(cyclooctadiene)nickel ($Ni(COD)_2$) and $TePR_3$.[2] They isolated and crystallographically characterized two intermediate clusters, $Ni_9Te_6(PEt_3)_8$ (**1**) and $Ni_{20}Te_{18}(PEt_3)_{12}$ (**2**).

along which the structures of the clusters can be deformed to give direct, excised fragments of NiTe; and (3) show, using model calculations of the extended Hückel type, the energy trends associated with the cluster to fragment distortion. These latter calculations indicate that the crystallographically determined structure of **1** is perhaps not the lowest enthalpy geometry of $L_8Ni_9Te_6$ (L = two electron donor ligand).

The idea that solid-state structures and discrete molecular clusters are related is hardly new; many researchers have suggested that clusters[3] may play an intermediary role in the routes to larger metal complexes and solid-state materials.[4] In particular, clusters

● Ni　　◯ Te　　◎ PEt_3

　　1　　　　　　**2**

In this paper we (1) show that **1** and **2** each bear a simple structural relationship to the NiTe extended solid; (2) show paths

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