and intramolecular hydrogen bonding involving the terminal oxo groups and the NH groups of the ligand[20] may also contribute, although in the present case this seems not to be the case since no such interactions are detectable in *syn*- or *anti*-$[L_2W_2O_4]^{2+}$.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support. Dr. P. Chaudhuri (Bochum) is thanked for helpful suggestions concerning the preparation of complexes.

Registry No. 1, 97414-60-3; 2, 114376-24-8; *syn*-$[L_2W_2O_4]I_2$, 97373-51-8; LWO_3, 108344-95-2; $[L_2W_2O_5](Br_3)_2$, 114299-76-2; Zn, 7440-66-6.

Supplementary Material Available: Tables S1–S4, listing anisotropic thermal parameters and calculated positions of hydrogen atoms (2 pages); tables of calculated and observed structure factors for *anti*-$[L_2W_2O_4]I_2$ and *syn*-$[L_2W_2O_4]_2(S_2O_6)I_2{\cdot}2H_2O$ (13 pages). Ordering information is given on any current masthead page.

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Optical Absorption and Luminescence Spectroscopy of $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$ and $[LCr(OH)(CH_3COO)_2ZnL](ClO_4)_2{\cdot}0.5H_2O$ (L = 1,4,7-Trimethyl-1,4,7-triazacyclononane)

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The optical spectroscopic properties of the title compounds were investigated by single-crystal absorption and luminescence spectroscopy as well as luminescence decay measurements between 1.8 K and room temperature. With a luminescence line-narrowing technique, accurate values for the ground-state exchange parameters were determined for $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$, with L = 1,4,7-trimethyl-1,4,7-triazacyclononane: $J = -14.6$ cm^{-1} and $j = 0.1$ cm^{-1} with $\hat{H}_{ex} = -2J(\vec{S}_1{\cdot}\vec{S}_2) - j(\vec{S}_1{\cdot}\vec{S}_2)^2$. The emitting state is shown to have $S = 1$. In $[LCr(OH)(CH_3COO)_2ZnL](ClO_4)_2{\cdot}0.5H_2O$ the presence of nonradiative transfer of excitation energy between crystallographically inequivalent dinuclear units is established. A simple kinetic model is able to quantitatively account for the observed luminescence decay behavior.

1. Introduction

The optical spectroscopic properties of chromium(III) compounds have continuously been the subject of intensive study for more than 2 decades.[2,3] The main interest among coordination chemists is in the understanding of the photochemical properties of chromium (III) complexes.[4] In the solid-state sciences one of the main emphases is on chromium(III)-doped crystals and glasses as possible candidates for new laser materials.[5] Understanding the relaxation and energy-transfer processes is very important for designing new solids suitable for application as lasers. The study of exchange-coupled chromium(III) pairs, which has been an active area of research for some time, has both chemically and physically relevant aspects.[6,7] Besides the synthesis of new compounds, one of the main aims has been the establishment of correlations between various physical properties and the structure.[8]

The tridentate chelate ligand L = 1,4,7-trimethyl-1,4,7-triazacyclononane has opened the way to a new family of dinuclear complexes. $[LCr(OH)_3CrL]^{3+}$ was the first trihydroxo-bridged chromium(III) complex to be synthesized.[9] Variation of the metal ions in this dinuclear unit is possible, and both homonuclear and heteronuclear complexes have been prepared.[10] Another possibility is the variation of the bridging ligands and the bridging geometry. The title compounds $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$ (abbreviated {CrCr}) and $[LCr(OH)(CH_3COO)_2ZnL](ClO_4)_2{\cdot}0.5H_2O$ (abbreviated {CrZn}) have been synthesized very recently.[10] They exhibit a new type of triply bridged dinuclear structure. {CrCr} has been magnetochemically characterized, and a value for the exchange parameter, $J = -15.5$ cm^{-1}, based on the Hamiltonian of eq 1, has been estimated from the temperature dependence of the powder magnetic susceptibility.[10]

The study of exchange interactions in triply bridged chromium(III) pairs is relatively new, and only a few investigations have been reported.[11-13] The optical spectroscopic properties of $[LCr(OH)_3CrL](ClO_4)_3$ have been studied in great detail.[11] High-resolution single-crystal spectroscopy down to 1.5 K turned out to be very informative, and the mechanism of the exchange coupling could be elucidated in detail. In the present study we use spectroscopic techniques, which are well-established in the field of chromium(III)-doped systems but which have only scarcely been applied to pure coordination compounds. The technique of luminescence line narrowing provides a very accurate picture of the first excited state and the exchange splittings in the ground state of {CrCr}. Singly ({CrCr} and {CrZn}) and doubly ({CrCr}) excited states are explored by single-crystal absorption spectroscopy. The comparison of {CrCr} and {CrZn} in the region of ^2E and $^2T_1$ excitations allows an estimate of the various contributions to the observed spectroscopic splittings. {CrZn} is shown to have two crystallographically inequivalent dimer sites. Excitation energy transfer between the sites takes place as a result of weak intermolecular interactions. Time-resolved and site-selective laser spectroscopies provide the necessary data for a quantitative understanding of these phenomena.

The spectroscopic methods used in this study are highly selective. In contrast to bulk techniques, they provide access to the

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properties of individual molecular species in the crystal.

2. Experimental Section

The synthesis and chemical analysis of the title compounds are reported in ref 10. Single crystals with edges of up to 1 mm length were grown by slow evaporation of saturated aqueous solutions over 3–5 days. The dark red crystals showed pronounced extinction directions under a polarizing microscope.

Powder X-ray diffraction measurements were performed on both title compounds with a Guinier camera using Cu Kα_1 radiation. {CrZn} showed a diffraction pattern identical with the calculated[14] pattern for the analogous {CrCo} compound whose structure has been determined.[10] The crystal structure of {CrCr} is unknown.

Absorption spectra were recorded on a Cary 17 spectrophotometer equipped with a pair of Glan–Taylor prisms. The crystals were cooled in a closed-cycle helium cryostat (Air Products CSA 202-G). Low-resolution luminescence spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrometer. Sample cooling was achieved with a helium-flow cryostat (Oxford Instruments CF 204). High-resolution luminescence spectra were recorded as follows: The 514.5-nm line of an Ar^+ ion laser (Spectra Physics 166, 5 W) was used for sample excitation. For the narrowed spectra a dye laser (Spectra Physics 375; bandwidth 30 GHz; DCM Exciton dye in 2:3 propylene carbonate/ethylene glycol pumped with the Ar^+ ion laser) was used as excitation source. The emitted light was dispersed by a 0.85-m double monochromator (Spex 1402) and detected by a cooled photomultiplier (RCA 31034) in conjunction with a photon counting system (Spex DPC-2). Cooling of the crystals down to 1.8 K was achieved with a liquid-helium-bath cryostat (Oxford Instruments MD4). Luminescence decay curves were measured with a pulsed dye laser (Molectron DL-100, pumped with a Molectron LN-14 nitrogen laser; 10-ns pulse width) for excitation, a 1-m monochromator (Spex 1704X) for dispersion, and a cooled photomultiplier (RCA 31034) for detection. The time dependence of the signal was recorded with a multichannel analyzer (EG&G ORTEC 7100). The crystals were cooled in a liquid-helium-bath cryostat (Thor S-100). A more detailed description of this setup can be found in ref 15.

3. Spectroscopic Results

The intense spin-allowed d–d transitions of the chromium(III) centers in the title compounds give rise to very similar absorption spectra for solutions[10] and crystals of {CrCr} and {CrZn}. Although the coordination of the chromium(III) ions strongly deviates from a regular octahedron, the two observed spin-allowed transitions can be assigned in octahedral symmetry. In the following the spin-forbidden transitions observed in more detailed spectra will be labeled in this idealized symmetry also.

Figure 1 shows absorption spectra of {CrZn} in the region of the lowest energy $^4A_2 \rightarrow {}^2E, {}^2T_1$ transitions. The same spectral region of ^2E and $^2T_1$ single excitations is shown for {CrCr} in Figure 2. Without making any analysis at this point, it is striking that the spectrum of {CrCr} shows a larger number of transitions than the spectrum of {CrZn}. The total energy spread of the absorption bands is larger in {CrCr} (1200 cm^{-1}) than in {CrZn} (850 cm^{-1}). These features are both the result of exchange interactions in {CrCr} and are discussed in more detail in section 4.1. The bands in the {CrCr} spectrum are more intense than the {CrZn} bands by approximately a factor of 5. An interpretation is given in section 4.3.

At temperatures below 200 K both compounds show luminescence. Their emission spectra are included and compared with the absorption spectra in Figures 1 and 2. In {CrCr} at 22 K the dominant luminescence peak centered at 14 275 cm^{-1} corresponds to the lowest energy absorption peak. The prominent hot band at 89 cm^{-1} higher energy in luminescence (135 K) corresponds nicely to the second absorption maximum as indicated by the dotted lines in Figure 2. In Figure 1 an analogous correspondence of the most intense luminescence and the lowest energy absorption peaks (centered at 14 094 and 14 173 cm^{-1}) can be seen for {CrZn}. Therefore the prominent luminescence bands for both compounds are purely electronic transitions. The lack of mirror symmetry between luminescence and absorption spectra clearly shows that all the dominant higher energy absorption bands are electronic and not vibronic in origin.

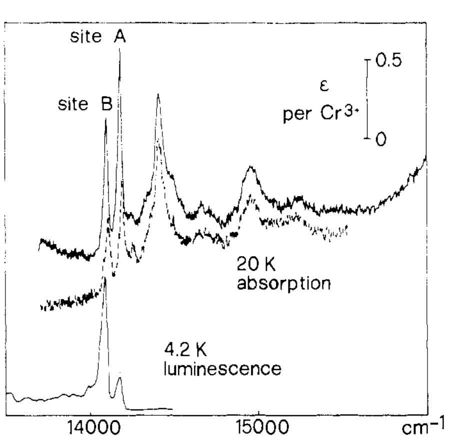

Figure 1. Absorption (polarized along the extinction directions of the crystals, which are undefined with respect to molecular orientations) and unpolarized luminescence spectra of $[LCr(OH)(CH_3COO)_2ZnL](ClO_4)_2 \cdot 0.5H_2O$ in the region of lowest energy transitions. Labels A and B denote transitions of the two crystallographically inequivalent molecular units.

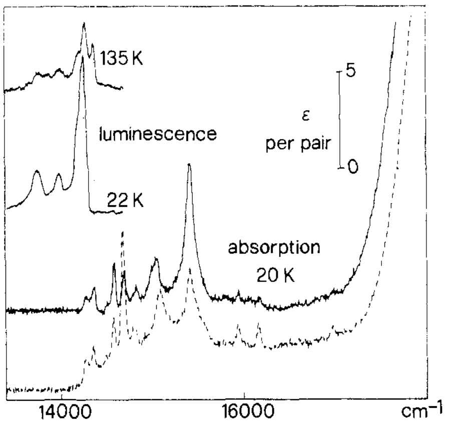

Figure 2. As for Figure 1, but containing the spectra of $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$. The coincidence of electronic origins in absorption and luminescence is indicated by the dotted lines.

The occurrence of two distinct electronic origins (labeled A and B in Figure 1) separated by 79 cm^{-1} in the absorption and luminescence spectra of {CrZn} is the result of two sets of molecular units occupying inequivalent crystallographic positions. The splitting of the ^2E excited state is smaller than the bandwidth and thus unresolved. {CrZn} has the same powder X-ray pattern as the analogous {CrCo} and {CrFe} compounds, and in this triclinic structure (space group $P\bar{1}$), two equally occupied sites for the dinuclear complexes have been found by X-ray diffraction.[10] For {CrCo} and {CrFe}, bond lengths and angles of the inequivalent molecular units differ by less than 1%. If similar small differences obtain for {CrZn}, they could lead to the 79-cm^{-1} separation of the $^2E \leftrightarrow {}^4A_2$ transitions for the two complexes in {CrZn}. In view of the transition energy of approximately 14 000 cm^{-1}, this is a very small difference and can be observed only due to the occurrence of sharp bands. The two lines A and B have comparable intensities in the absorption spectrum as expected from the crystal structure. In luminescence their intensities are different, with line B being dominant. This observation can be rationalized by taking into account nonradiative transfer of excitation energy between the two sites. Luminescence decay curve measurements are the method of choice to study such transfer processes. In Figure 3 we present the luminescence decay curves at two selected temperatures measured at the maximum of the origins for sites A and B, as indicated in the insert. For site A a higher deactivation rate is observed than for site B at both temperatures, in agreement with the observed luminescence intensity ratio. Some deviations from exponential behavior are observed within the first 500 μs after the excitation pulse. At times longer than 500 μs the curves are exponential. The lifetimes derived from this part of the curves

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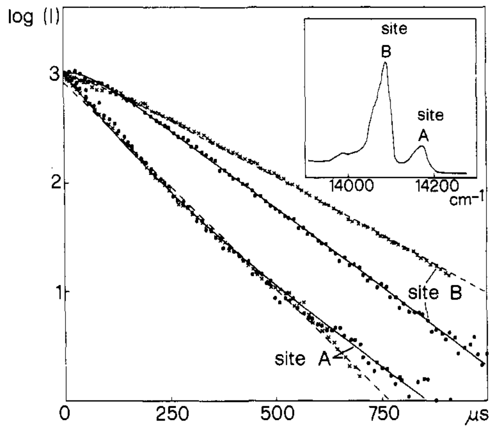

Figure 3. Luminescence decay curves of $[LCr(OH)(CH_3COO)_2ZnL](ClO_4)_2\cdot0.5H_2O$ at two selected temperatures. Crosses denote measurements at 12 K with fits to eq 3 and 4 shown as dashed lines. Circles represent measurements at 55 K with the corresponding fits drawn as solid lines. The decay curves for sites A and B were measured at the peak energies of the luminescence origins shown in the inset.

are clearly different for site A and B at 12 K, but at 55 K they are the same within experimental accuracy. Analysis of all these features with a simple donor/acceptor model is possible and will be presented in section 4.2.

The luminescence peak of {CrCr} shown in Figure 2 has a width of approximately 110 cm^{-1}. It is thus too broad to yield information about ground-state electronic splittings due to exchange interactions. This is a situation often encountered with chromium(III) coordination compounds. The broadness of the observed bands is usually, as in the present case, inhomogeneous, i.e. due to the presence of slightly different subsets of chromophores with small variations in transition energy. The observed spectrum is therefore a superposition of all the spectra of different subsets, leading to a loss of information. To overcome this inhomogeneous broadening, the technique of luminescence line narrowing has been developed and applied to doped crystals and glasses for several years.[16] In the very recent past it has been shown to be a useful technique also for pure coordination compounds.[11,13,17] When a narrow-bandwidth dye laser within the lowest energy absorption band profile is used, a small subset of chromophores is selectively excited. In the absence of energy transfer a narrowed luminescence spectrum corresponding to this subset is then observed. Narrow-band excitation in slightly higher energy absorption bands leads to broadened luminescence spectra since electronic origins and vibronic sidebands of many subsets overlap, thus reducing the selectivity of the technique. Excitation energy-transfer processes among the various subsets within the lifetime of the excited state lead to line broadenings as well. In order to minimize these transfer processes, we found it necessary to work at temperatures below 4.2 K for {CrCr}. In Figure 4 we present line-narrowed luminescence spectra at 1.8 K in the electronic origin region together with a nonselectively excited luminescence spectrum. The reduction in luminescence line widths is from approximately 110 to about 5 cm^{-1}. Up to now, this is the most dramatic luminescence line-narrowing effect reported for a pure crystalline coordination compound. Bands that are completely unresolved in the nonselectively excited spectrum appear as single sharp lines. The narrowed luminescence spectrum is different for different excitation wavelengths within the absorption band profile (spectra a and b in Figure 4). The shift observed for the major luminescence lines corresponds to the shift of the excitation line. From a comparison of all the narrowed luminescence spectra as the excitation is scanned through the first absorption band, it is possible to unambiguously identify the intrinsic features of the {CrCr} dimers. They are labeled 0, 1, and 2, according to the ground-state dimer levels they belong to. The additional weak lines with intensities strongly dependent on excitation energy are most likely due to an impurity that is accidentally excited at the laser frequency. In contrast to bulk techniques like magnetic susceptibility measurements, the analysis of our spectroscopic experimental data is not affected by the presence of a small amount of impurity. The results of our analysis are presented in section 4.1.

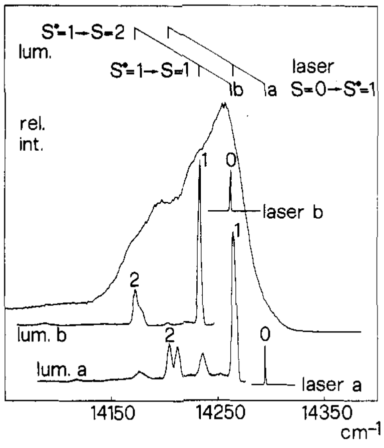

Figure 4. Detailed luminescence spectra of $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$ at 1.8 K in the region of the electronic origins. Top trace: unselective excitation at 514.5 nm (Ar$^+$ ion laser). Bottom traces: narrowed luminescence spectra for two different dye laser wavelengths *a* and *b*. Electronic origins are labeled with the ground-state dimer spin *S*. Band assignments and ground-state splitting patterns for the two subsets *a* and *b* are given on the top.

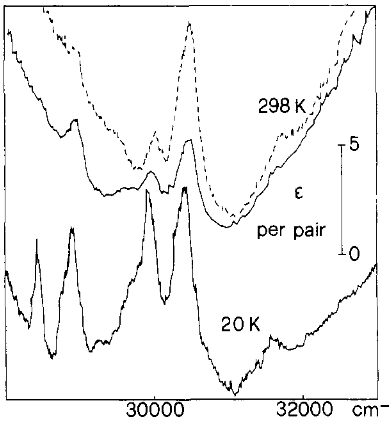

Figure 5. Polarized absorption spectra of $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$ in the region of double excitations $^4A_2{}^4A_2 \rightarrow {}^2E^2E$, $^2E^2T_1$, and $^2T_1{}^2T_1$.

Another typical manifestation of exchange interactions in the absorption spectrum of {CrCr} is the occurrence of bands at roughly twice the energy of the lowest energy absorptions, as shown in Figure 5. These transitions correspond to the double excitations $^4A_2{}^4A_2 \rightarrow {}^2E^2E$, $^2E^2T_1$, and $^2T_1{}^2T_1$. Their positions are close to twice the energy of the lowest sharp absorption bands. The first double excitation maximum lies at 28 450 cm^{-1}, which is almost exactly twice the energy of the first single excitation at 14 274 cm^{-1}. Their total energy spread of 2100 cm^{-1} is also close to twice the range of the single excitations (1200 cm^{-1}). The double excitations lose their intensity with increasing temperature as shown in Figure 6.

4. Discussion

4.1. Exchange Interactions in $[LCr(OH)(CH_3COO)_2CrL](ClO_4)_3$.

(a) Ground State. The splitting of the $^4A_2{}^4A_2$ ground state of a dinuclear chromium(III) complex due to exchange interactions between the two ions is a well-known effect.[6,7] Since the ground-state magnetic moment of chromium(III) is spin-only to a good approximation, a Heisenberg operator, eq 1, provides

$$\hat{H}_{ex} = -2J(\vec{S}_1\cdot\vec{S}_2) - j(\vec{S}_1\cdot\vec{S}_2)^2 \qquad (1)$$

an adequate description for the pair ground state. The first term

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(16) *Laser Spectroscopy of Solids*; Yen, W. M., Selzer, P. M., Eds.; Springer Topics in Applied Physics 49, Springer: West Berlin, 1981.

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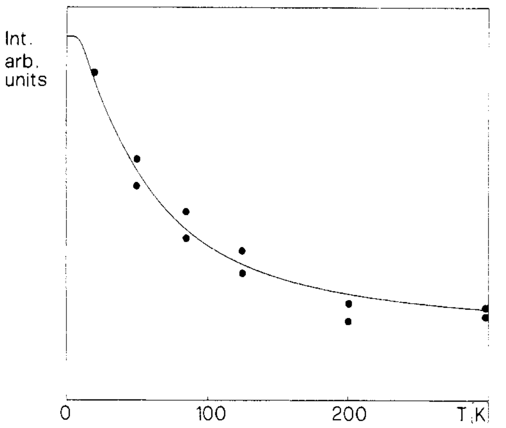

Figure 6. Temperature dependence of the total intensity of the double-excitation transitions shown in Figure 5. The solid line is calculated with eq 2 by using a fitted scaling factor.

Table I. Energies of Narrowed Luminescence Transitions[a]

excitation energy (laser), cm^{-1}	luminescence transitions, cm^{-1}			
$S = 0 \rightarrow S^* = 1$	$S^* = 1 \rightarrow S = 1$	$S^* = 1 \rightarrow S = 2$	J, cm^{-1}	j, cm^{-1}
14 261.8	14 232.2	14 173.5	-14.5	0.1
14 292.5	14 262.8	14 203.9	-14.6	0.1
14 293.6	14 263.0	14 203.3	-14.5	0.2
14 294.4	14 264.3	14 204.8	-14.7	0.1
14 299.3	14 268.8	14 208.8	-14.7	0.2

[a] The exchange parameters J and j were determined by using the eigenvalues of eq 1.

in eq 1 leads to a Landé pattern with S, the total spin quantum number of the pair, ranging from 0 to 3. The second, biquadratic term causes small deviations from this pattern. For negative values of J, i.e. antiferromagnetic exchange coupling, the pair level with $S = 0$ is lowest in energy.

It is quite clear that no information about exchange splittings can be obtained from the nonselectively excited luminescence spectrum in Figure 4. The bandwidth is larger than the energy separations expected on the basis of eq 1 with a J value of approximately -15 cm^{-1}.[10] As a result of the extreme reduction in line width, the situation is much more favorable in the narrowed luminescence spectra. At 1.8 K the $S = 0$ ground-state pair level is the only one with an appreciable population. The dye laser is tuned to match the energy difference between this level and the lowest pair level of the first excited state for a given subset. This transition is denoted $S = 0 \rightarrow S^* = 1$ in Figure 4. Assignment of the first excited level as $S^* = 1$ is possible on the basis of the relative intensities in the luminescence lines. The dominant line is readily assigned as the spin-allowed $S^* = 1 \rightarrow S = 1$ transition. The $S^* = 1 \rightarrow S = 2$ transition is also observable, but the doubly spin forbidden $S^* = 1 \rightarrow S = 3$ transition could not be measured. The positions of the exciting laser line and the two luminescence lines thus fully determine the exchange splitting and the exchange parameters J and j. The values obtained for various subsets are collected in Table I. Obviously there is no systematic variation of J and j with excitation energy; not even excitation at the extreme low-energy side of the first absorption band yields differing values, as can be seen from the first row of Table I. A systematic variation of J and j with excitation energy has been observed in [(bispicam)Cr(OH)$_2$(SO$_4$)Cr(bispicam)]$S_2O_6 \cdot 3H_2O$ (bispicam = bis(2-pyridylmethyl)amine),[13] another triply bridged chromium(III) coordination compound. We conclude that in {CrCr}, despite the extreme inhomogeneous broadening, all of the complexes within the distribution of sites in the crystal have nondistinguishable exchange parameters.

The J value for {CrCr} of -14.6 cm^{-1} is comparable to the value of -15.5 cm^{-1} obtained from the magnetic susceptibility measurements. This is interesting, because there was a rather high amount of paramagnetic impurity in the powder sample used. The j value of -0.9 cm^{-1} and the g value of 2.16 reported in ref 10 on the basis of the magnetic susceptibility measurements are physically unreasonable. Thus, for {CrCr} a poor least-squares fit of magnetic susceptibility data provides quite a reasonable J value. The same is not true for j, which comes out too large and with the physically wrong sign. The spectroscopic j is small and positive as expected.

An independent confirmation of the ground-state exchange parameters is possible from the absorption spectra. As shown in Figures 5 and 6, the relatively sharp bands in the near-UV region show a pronounced temperature dependence. They are transitions to $^2E^2E$, $^2E^2T_1$, and $^2T_1{}^2T_1$ doubly excited pair levels with a total spin of either 0 or 1. Assuming an exchange-induced intensity mechanism with $\Delta S = 0$[18] as spin selection rule, transitions to doubly excited states are possible only from the lowest energy ground state components with $S = 0$ and 1. Their intensity can be expressed as

$$I = K(P_{S=0} + 0.555P_{S=1}) \qquad (2)$$

where K is an adjustable scaling factor, $P_{S=0}$ and $P_{S=1}$ are the Boltzmann factors, and 0.555 is the theoretical ratio of the two transition probabilities.[18] The Boltzmann factors can be calculated from the known exchange parameters $J = -14.6$ cm^{-1} and $j = 0.1$ cm^{-1}; therefore, only the scaling factor has to be adjusted to fit the data. The agreement is excellent, as shown in Figure 6. While this is an independent check of J, the parameter values derived from the narrowed luminescence spectra are far more accurate.

(b) Singly Excited States. A characterization of the lowest excited pair states $^2E^4A_2$ and $^2T_1{}^4A_2$ can be made on the basis of both absorption and luminescence spectra. The lowest energy excited level, from which luminescence is observed, has a spin $S^* = 1$. This is unambigously deduced from the line-narrowed and the nonselectively excited luminescence spectra, which both show that the $S^* = 1 \rightarrow S = 1$ transition has highest intensity. A prominent hot band is observed in an emission positioned 96 cm^{-1} higher than the maximum of the cold band. On the basis of its intensity, it is also likely to be a $S^* = 1 \rightarrow S = 1$ transition. As indicated by the dotted lines in Figure 2, the corresponding absorption origins are observed as well. A detailed assignment of the higher energetic electronic origins in the absorption spectra is not possible, mainly due to the relatively broad transitions, the unknown crystal structure, and the low molecular symmetry. In another triply bridged dinuclear chromium(III) compound, [LCr(OH)$_3$CrL](ClO$_4$)$_3$ (abbreviated {triol}), which has a hexagonal crystal structure and very sharp, polarized absorption and luminescence transitions, a complete analysis of the single excitations has been made.[11] We can draw some important conclusions by comparing the spectroscopic properties of this compound with those of {CrCr}. The lowest energy excited pair level of {triol} has $S = 1$, identical with that for {CrCr}. On the other hand, all the mono- and bis(μ-hydroxo)-bridged chromium(III) pairs studied with optical spectroscopy so far have a lowest excited level with $S = 2$. From this we conclude that exchange interactions in {CrCr} are similar to those in {triol}; i.e., the acetate bridging ligands provide important exchange pathways, and the OH bridge does not dominate the picture. The exchange coupling in {CrCr} is thus clearly different from that in a mono(μ-hydroxo)-bridged complex such as [(NH$_3$)$_5$CrOHCr(NH$_3$)$_5$]Cl$_5 \cdot$H$_2$O,[17] although the latter has ground-state exchange parameters of $J = -15.3$ cm^{-1} and $j = 0.3$ cm^{-1}, practically identical with those of {CrCr}. Comparing only the numerical values for J and j could therefore easily lead to a wrong conclusion in the present case. The essential additional information is provided by absorption and luminescence spectroscopy.

The total spread of the observed $^2E^4A_2$ and $^2T_1{}^4A_2$ absorptions in {triol} is 1900 cm^{-1}, while for {CrCr} it is 1200 cm^{-1}. This spread is determined by both the single-ion energies of the ^2E and $^2T_1$ components and exchange interactions in these excited states. In

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{CrCr} this energy range is determined mainly by the single-ion energies, whereas in {triol} the strong exchange interactions give the dominant contribution. The total intensities of the $^2E^4A_2$ and $^2T_1{}^4A_2$ single excitations are temperature independent. This leads to the conclusion that there is a dominant single-ion-intensity mechanism, similar to that for $Cs_3Cr_2Cl_9$.[19]

4.2. Excitation Energy Transfer in $[LCr(OH)(CH_3COO)_2ZnL](ClO_4)_2 \cdot 0.5H_2O$. As shown in section 3, there are two crystallographically inequivalent dinuclear units in {CrZn} and energy-transfer processes are evident from the spectroscopic data. This is an attractive situation to study the nonradiative transfer of excitation energy between sites A and B in some detail. A special advantage of the present situation lies in the fact that there is no need for doping traps into the material; i.e., energy transfer in the *unperturbed* {CrZn} compound can be studied. Up to now, there are only few examples of work on such concentrated systems.[17,20,21]

The luminescence decay curves in Figure 3 show clear evidence for energy transfer. The higher energy site, denoted A, acts mainly as a donor; the lower energy site, B, acts mainly as an acceptor of excitation energy. This qualitative conclusion is supported by the luminescence intensity ratios of the electronic origins for sites A and B.

In order to obtain a quantitative picture of the processes involved, we use a phenomenological model. Similar kinetic schemes are presented in ref 16 and 22. As parameters we have two transfer rates: k_t for the step from the higher energy site A to site B and k_{bt} for the back-transfer step from B to A. Further we take into account k, the relaxation rate of a single molecular unit. This rate is assumed to be identical for sites A and B since the two sites are crystallographically and spectroscopically very similar. Because we did not use a selective excitation technique, we have to take into account pumping rates W_A and W_B for direct excitation of the two sites A and B, respectively. The rate equations for this energy-transfer model are given by

$$dn_A/dt = W_A - kn_A - k_tn_A + k_{bt}n_B \tag{3}$$

$$dn_B/dt = W_B - kn_B - k_{bt}n_B + k_tn_A \tag{4}$$

with n_A and n_B denoting the number of chromium(III) ions of each type in the lowest excited state. Equations 3 and 4 were solved numerically for δ-pulse excitation, and for a given temperature, they were simultaneously fitted to the luminescence decay curves for both sites.[23] The resulting fits are very good; examples for temperatures of 12 and 55 K are given in Figure 3.

The divergence of the A and B curves for long times at 12 K is clear evidence that back-transfer is still negligible at this temperature. The nonradiative feeding is a one-way A → B process. We can obtain a check of the validity of our procedure by the following comparison. The 12 K slope of the exponential decay curve for site A, 11 530 s^{-1}, is equal to the sum of the rates for A → B transfer (k_t) and the deactivation rate of site A (k). The values obtained from a fit of eq 3 and 4 to the complete data set at 12 K are $k_t = 10090 \pm 1600\ s^{-1}$, $k = 4652 \pm 860\ s^{-1}$, and $k_t + k = 14740 \pm 1900\ s^{-1}$. The agreement of the two numbers is satisfactory, and we conclude that eq 3 and 4 provide an adequate description of the physical situation.

At 55 K the situation is quite different. The curve for site A shows a slower decay for $t > 500\ \mu s$ than in the 12 K measurement for the same site. This is a clear manifestation of energy back-transfer. It is interesting to note that the 55 K curves run parallel at times larger than 500 μs. At these times transfer and back-transfer processes are in a dynamic equilibrium, leading to a steady n_A/n_B population ratio. The relaxation of the single molecular units governs the observed behavior. We can take the identical steepness of the 55 K curves for sites A and B as a confirmation of our assumption that the individual decay rates of the two sites are identical. But caution is necessary here, because very fast A ↔ B energy-transfer processes could cause the same effect. From Figure 7 we find for 55 K that $k_t \cong 3k$ and $k_{bt} \cong 0.2k$; i.e., the transfer rates have the same order of magnitude as the individual decay rates and could thus partially be responsible for the observed identical steepness.

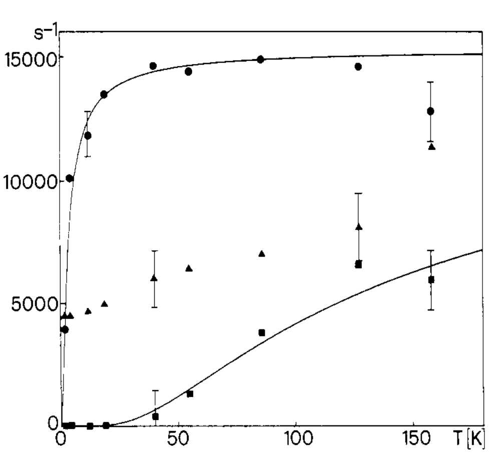

Figure 7. Rates for energy transfer (k_t, site A → site B, circles), back-transfer (k_{bt}, site B → site A, squares), and the intramolecular deactivation rate (k, triangles) as a function of temperature. k_t, k_{bt}, and k are defined in eq 3 and 4. The solid lines are fits to eq 5.

The transfer (k_t), back-transfer (k_{bt}), and the intramolecular deactivation (k) rates obtained in the above procedure are plotted in Figure 7 as a function of temperature. The simplest way to rationalize the behavior of k_t and k_{bt} is by an Arrhenius equation:

$$k_{t/bt}(T) = k_{t/bt}(T \rightarrow \infty)\ e^{-\Delta E_{t/bt}/kT} \tag{5}$$

The fits of this equation to the observed rates are excellent, as can be seen from Figure 7. The resulting parameter values are $1.7 \pm 0.6\ cm^{-1}$ and $85 \pm 3\ cm^{-1}$ for ΔE_t and ΔE_{bt}, respectively, and $15300 \pm 500\ s^{-1}$ and $14200 \pm 700\ s^{-1}$ for $k_t(T \rightarrow \infty)$ and $k_{bt}(T \rightarrow \infty)$, respectively. Such activation energies obtained from Arrhenius-type equations are easily overinterpreted when compared to microscopic energy differences. Nevertheless we notice that the transfer step from A to B has a very small but nonzero activation barrier and the reverse step from B to A has an activation energy very close to the sum of the energy difference between the electronic origins of the two inequivalent sites (79 cm^{-1}) and the activation energy for the A → B transfer step (1.7 cm^{-1}). It therefore appears that in {CrZn} we have a situation which corresponds to the simplest possible picture for an energy-transfer and energy-back-transfer situation: two energy levels separated by 79 cm^{-1} and an activation barrier of 1.7 cm^{-1} in height. The phenomenological kinetic model in eq 3 and 4 turns out to be an adequate description of the energy-transfer processes in {CrZn}.

4.3. Comparison between {CrCr} and {CrZn}. In this section the spectroscopically evident inhomogeneities, the absorption intensity mechanisms, and the relaxation pathways in {CrCr} and {CrZn} are discussed.

The line-narrowing experiments in {CrCr} unambiguously prove the inhomogeneous nature of the band widths in the unselectively excited luminescence spectrum. Further, in the line-narrowed spectra all luminescence lines are about 5 times broader than the laser excitation profile as seen in Figure 4. The luminescence line width is thus essentially inhomogeneous even in the narrowed spectra at 1.8 K. This is clear evidence for excitation energy transfer from the excited subset of chromophores to energetically very close but different molecular units. This type of spectral energy transfer and its related phenomena have been widely studied in lanthanide-doped glasses.[24] Since absorption spectroscopy is not a site-selective technique, the width of the lowest

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energy transition, 40 cm^{-1} for {CrCr}, is also inhomogeneous, similar to that for the unselectively excited luminescence spectrum.

When the absorption spectra in the region of ^2E and $^2T_1$ excitations (Figures 1 and 2) are compared, it is striking that ϵ values are up to 5 times larger for {CrCr} than for {CrZn}. Since in both systems the transitions gain most of their intensities by a single-ion mechanism, we feel that the different behavior is due to the charge difference between the chromium(III) and zinc(II) neighbors of a given chromium(III). The higher charge of the neighbor gives rise to a larger electrostatic potential of ungerade parity at the site of the chromium(III) center, thus increasing the electric dipole transition moment of the otherwise parity-forbidden transitions. Different Cr–O and Cr–N distances in the molecular units may also contribute to the observed intensity differences.

Another interesting property to compare for {CrCr} and {CrZn} are the relaxation pathways for excited molecular units. There are essentially three possible mechanisms: (i) radiative relaxation, (ii) nonradiative multiphonon relaxation, and (iii) transfer of excitation energy to impurities and crystal imperfections acting as "killer" traps. These latter centers are excited by multistep nonradiative energy transfer from the genuine species and relax either nonradiatively or by emitting infrared photons.

(i) The radiative relaxation rate can be calculated from the observed oscillator strength of the lowest energy absorption origin and its vibrational sidebands.[25] The estimated values for the radiative lifetimes are on the order of 20 and 3 ms for {CrZn} and {CrCr}, respectively. They are 2 orders of magnitude longer than the measured lifetimes at 4.2 K: 230 μs for {CrZn} and 72 μs for {CrCr}. We conclude that radiative processes are not rate-determining and that quantum yields are of the order of 1% at 4.2 K.

(ii) Multiphonon relaxation rates are difficult to estimate, even for very simple high-symmetry complexes.[26] Here we only provide a qualitative argument, by which the observed faster decay of {CrCr} by a factor of 3 can be rationalized. It has been experimentally shown[27,28] that the number of high-energy vibrators in the immediate environment of the excited center is an important determinant for multiphonon relaxation rates. O–H and C–H stretching vibrations are the dominating accepting modes in the title compounds. Their numbers are the same for the dimeric molecules in {CrCr} and {CrZn}. The essential difference is that in {CrZn} the electronic excitation is localized on the chromium(III) side of the molecule, whereas in {CrCr} it is delocalized over the whole molecule as a result of exchange interactions. In other words, the excited center has a larger spatial extension in {CrCr}, and as a consequence, a larger number of high-energy vibrators can contribute to the multiphonon relaxation process.

(iii) Nonradiative energy transfer to "killer" sites is assumed to occur with a rate determined by the rate of excitation energy migration within the genuine chromophores. It is obvious from Figure 7 that below 50 K the energy-transfer rate k_t in {CrZn} is higher than k, the reciprocal of the lifetime, by a factor of about 3. k is therefore not likely to be determined by trapping of the excitation at "killer" sites. The same conclusion is drawn for {CrCr} based on decay measurements over the inhomogeneously broadened luminescence origin region.

In conclusion, the comparative study of {CrCr} and {CrZn} has led to a deeper understading of the manifestations of exchange interactions in {CrCr}. In addition energy-transfer processes resulting from intermolecular interactions as well as nonradiative relaxation processes have been elucidated.

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d^{10}–d^{10} Interactions: Multinuclear Copper(I) Complexes

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The unusual linear trinuclear Cu(I) complex [Cu(tolylNNNNNtolyl)]$_3$, synthesized by Beck and Strähle, contains a remarkably short Cu–Cu separation of 2.35 Å. This makes it the natural subject of a molecular orbital investigation which is presented in this paper. The Cu–Cu interaction is attractive, as a result of s + p_z + d_{z^2} mixing, as for other d^{10} complexes. The stereochemical requirements of the ligand (we make a distinction between geometrical and electronic bite size) also favor the very short Cu–Cu separation. We also studied the hypothetical oligomers $Cu_3(RN_5R)_4^-$ and $Cu_4(RN_7R)_4$ as well as extrapolated polymers $[Cu(N_2)_3]_\infty$ and $[Cu(N_2)_4]_\infty$. The latter should be conducting for most reasonable electron counts.

If the geometrical constraints of the ligand set allow it, Cu(I) complexes clearly express a tendency to cluster and polymerize.[1] The Cu–Cu distances observed in such oligomers and polymers range down to 0.2 Å shorter than the 2.56-Å separation in Cu metal. So the question is naturally raised as to the nature of the bonding interactions between Cu centers at such short distances. They cannot be repulsive. What could be done to make these Cu–Cu distances still shorter?

The answer to the first question has been given in our work and that of others:[2] there is mixing of 4s and 4p into 3d orbitals,

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