oxygen atoms, with slightly positive peaks near these atoms. This appearance is in contrast to that of the other hydrogen bond seen in the plane, O(W2)–H(21)···O(W3). Here the electron distribution is much more asymmetric with higher electron density near the hydrogen-bond acceptor atom O-(W3). Similar electron density distributions as in the bond O(W2)···O(W3) were observed in short *and* long hydrogen bonds of the water structure in picrylsulfonic acid tetrahydrate.[5]

References and Notes

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Triboluminescence and Pressure Dependence of the Photoluminescence of Tetrahedral Manganese(II) Complexes

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The triboluminescence of the tetrahedral manganese(II) complexes Mn(Ph$_3$PO)$_2$Cl$_2$, Mn(Ph$_3$PO)$_2$Br$_2$, (MePh$_3$P)$_2$MnCl$_4$, and (Et$_4$N)$_2$MnBr$_4$ is a superposition of the $^4T_1 \rightarrow {}^6A_1$ manganese-centered phosphorescence and a weak $^3\Pi_u \rightarrow {}^3\Pi_g$ emission from adsorbed molecular nitrogen. The triboluminescence and atmospheric pressure photoluminescence spectra are superimposable. The energy of the manganese-centered photoluminescence decreases linearly with pressure up to the maximum studied pressure of 42 kbars. The emitting manganese centers in the triboluminescence experiment are at atmospheric pressure. The applicability of previously proposed mechanisms to the manganese complexes is discussed in terms of the spectroscopic results.

Spectroscopic studies of triboluminescence (TL), the emission of light caused by the application of mechanical stress to crystals, have shown that the most common origins of the emission are crystal fluorescence,[1,2] crystal phosphorescence,[2,3] and emission from the second positive group of adsorbed nitrogen.[4,5] The oldest known triboluminescent substance is sugar[6] whose TL originates from adsorbed nitrogen.[5]

The first assignment of the TL of a transition metal complex was made by Cotton and Goodgame[7,8] for several tetrahedral manganese(II) complexes on the basis of the visual similarity of the colors of the photoluminescence and TL. These complexes are ideal candidates for spectroscopic study because the metal-centered transitions respond primarily to the ligands and less strongly to the intermolecular interactions which are important in the delocalized transitions of the π systems of aromatic organic molecules. We report here the TL spectra, the atmospheric pressure photoluminescence spectra, and the pressure dependence of the photoluminescence spectra of a series of tetrahedral manganese(II) complexes. Proposed TL excitation mechanisms are discussed in terms of the spectroscopic results.

Experimental Section

The TL was excited in all of the spectroscopic studies by grinding samples of approximately 0.5 g at room temperature in a Pyrex vial with a stainless steel rod. The TL could also be excited with grinding implements of other material such as wood, Teflon, or glass.

The TL spectra were measured with a Bausch and Lomb 1.0-m monochromator modified as shown in Figure 1 and EMI 9558 photomultipliers in Products for Research refrigerated housings. The TL emission from the sample mounted in a block was passed through
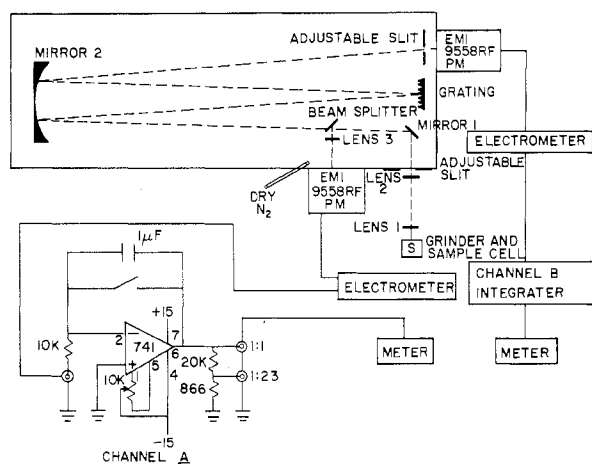
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Figure 1. Schematic design of the instrument used for measuring triboluminescence spectra.

Figure 2. Triboluminescence and room-temperature photoluminescence spectra of solid $Mn(Ph_3PO)_2Br_2$. The spectra are superimposed with emission maxima normalized to the same value.

Table I. Spectroscopic Results

Complex	Photoluminescence max, nm	Triboluminescence max, nm	Δ energy[a]/ Δ pressure, cm^{-1}/kbar	Emission lifetime,[b] μs
$Mn(Ph_3PO)_2Cl_2$	None	520		
$Mn(Ph_3PO)_2Br_2$	500	500	−31	602
$(MePh_3P)_2MnCl_4$	505	$(520 \pm 20)^c$	−39	155
$(Et_4N)_2MnBr_4$	515	515	−26	247
$(Bu_4N)_2MnI_4$	525	None	−41	
$(pyH)_2MnCl_4$	520	None	−20	

[a] Change in the energy of the luminescence maximum. [b] Solid state at room temperature. [c] Because of the low TL intensity, the position of the maximum could not be measured with the accuracy of the others.

collimating lenses 1 and 2 and an adjustable entrance slit into the monochromator. The beam, reflected from mirror 1, was intercepted by a quartz plate acting as a beam splitter. Approximately 12% of the total intensity was reflected through lens 3 to a cooled EMI 9558 photomultiplier. The total intensity of the polychromatic light measured here was referred to as I_T. A stream of dry nitrogen was blown over the face of this photomultiplier to prevent the buildup of moisture on the cooled surface. The remaining 88% of light intensity was passed through the monochromator and an adjustable exit slit to a second cooled EMI 9558 photomultiplier and was referred to as I_λ. The intensities of several TL pulses were simultaneously monitored by the two photomultipliers, amplified, integrated over two 1-μF capacitors, and read as I_T and I_λ. The intensity was normalized as $I = I_\lambda/I_T$. At least five separate readings were made at 5-nm intervals and the intensities were plotted vs. wavelength with error bars of one standard deviation of the readings.

All photoluminescence spectra at atmospheric pressure were recorded at room temperature with the same instrument used for obtaining the TL spectra. The compounds, contained in quartz vials, were excited by a 100-W high-pressure mercury arc lamp with the excitation wavelength selected by a Bausch and Lomb 0.25-m monochromator. A continuous-drive motor was attached to the wavelength dial of the emission monochromator and the emission was recorded on a strip chart recorder.

For the high-pressure emission studies, the sample was mixed 1:1 with NaCl and packed into a modified Drickamer Type I high-pressure optical cell.[9] The spectra were recorded with a Jarrell-Ash 0.5-m grating monochromator and a 1P28 photomultiplier. The samples were excited by the output of a 100-W mercury lamp filtered through distilled water and a Corning 7-54 filter. The error bars on the high-pressure data represent uncertainty in E_{max} due to slit width, scan speed, instrument pen rise time, and noise. All TL and photoluminescence spectra are uncorrected for instrument and photomultiplier response.
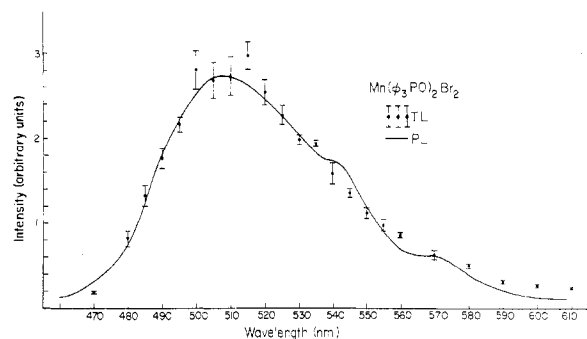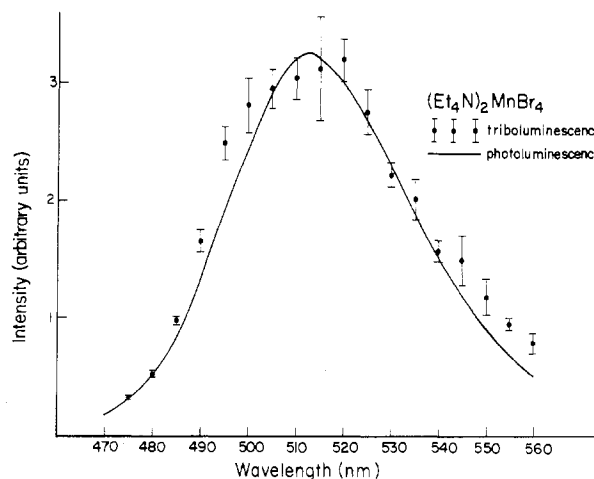

Figure 3. Triboluminescence and room-temperature photoluminescence of solid $(Et_4N)_2MnBr_4$. The spectra are superimposed with emission maxima normalized to the same value.

The manganese complexes were prepared according to the methods of Cotton et al.[7,8]

Results

Atmospheric Pressure Spectroscopy. Room-temperature photoluminescence spectra were measured for all of the solids listed in Table I except the nonphotoluminescent Mn-$(Ph_3PO)_2Cl_2$. No photoluminescence was observed from the latter compound even at liquid nitrogen temperature. The emissions from all of the photoluminescent compounds are in the green spectral region with maxima ranging from 500 to 525 nm as shown in Table I. Emission maxima in this wavelength region were previously measured from $((CH_3)_4N)_2MnBr_4$ and $((CH_3)_4N)_2MnCl_4$ and assigned to the $^4T_1 \rightarrow {}^6A_1$ transition.[10,11] The emissions observed in the compounds studied here are all undoubtedly from the same manganese-centered $(e)^3(t_2)^2 \rightarrow (e)^2(t_2)^3$ transition.

Triboluminescence spectra were measured for the four complexes indicated in Table I. Because the TL intensity from $((MePh_3)P)_2MnCl_4$ was very weak, its spectrum could not be measured as accurately as those of the other compounds. The TL spectra of $Mn(Ph_3PO)_2Br_2$ and $(Et_4N)_2MnBr_4$ at wavelengths longer than 470 nm are shown in Figures 2 and 3 superimposed on their respective photoluminescence spectra. On the basis of the similarity between the TL and the photoluminescence spectra, the TL is assigned to the same excited state as the photoluminescence. Strong TL was recorded from $(MePh_3P)_2MnCl_4$ although no photoluminescence could be observed. The TL spectrum, shown in Figure 4, has a maximum at 520 nm.

The TL spectra of all of the compounds contained a very weak series of bands between 300 and 370 nm with maximum
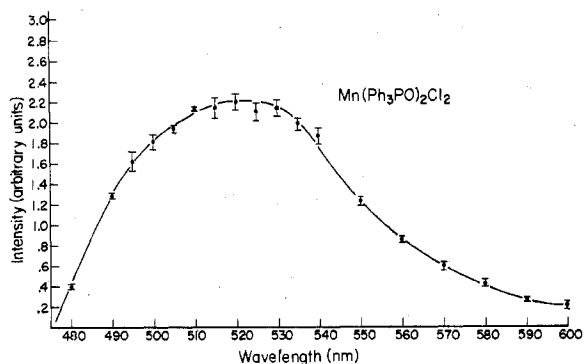
Figure 4. Triboluminescence spectrum of $Mn(Ph_3PO)_2Cl_2$.

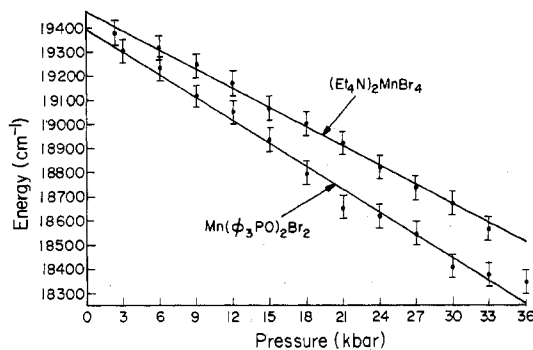**Figure 5.** Shift of emission energy with pressure for $Mn(Ph_3PO)_2$-Br_2 and $(Et_4N)_2MnBr_4$.

intensities less than one-hundredth of that of the manganese d–d emission between 500 and 525 nm. These bands have also been observed in the TL spectra of aniline hydrochloride[4] and sucrose[5] and were assigned to the $^3\Pi_u \rightarrow {}^3\Pi_g$ emission of molecular nitrogen. In order to verify the assignment of these bands in the tetrahedral manganese TL spectra, a sample of $Mn(Ph_3PO)_2Br_2$ was vacuum-degassed and the TL spectrum taken under argon. No lines between 300 and 370 nm were observed although the bright manganese-centered triboluminescence remained.

High-Pressure Spectroscopy. Emissions of the photoluminescent compounds were studied at hydrostatic pressures up to 42 kbars. The effects of pressure on the energies of the emission maxima of $Mn(Ph_3PO)_2Br_2$ and $(Et_4N)_2MnBr_4$ are shown in Figure 5. The plots of emission energy vs. pressure are linear within the range of pressures studied. All of the complexes show a decrease in emission energy with increasing pressure. The slopes range from −41 to −20 cm^{-1}/kbar and are listed in Table I.

Discussion

Assignment of the Luminescence. The d–d excited states of tetrahedral manganese(II) complexes have been assigned using ligand field theory.[8,10,11] The lowest energy excited state, $^4T_1$, arises from a $(e)^3(t_2)^2$ electronic configuration. The photoluminescence mirrors the low-energy $^4T_1$ absorption band and obeys exponential intensity decay with lifetimes on the order of 10^{-4} s.[10,11] For these reasons, the luminescence was assigned to the $^4T_1 \rightarrow {}^6A_1$ transition.[10] The mixed-ligand triphenylphosphine oxide complexes (C_{2v} symmetry) were treated as having approximately tetrahedral site symmetry. Their luminescences were assigned as above on the basis of the similar yellow-green colors.[7]

The photoluminescence maxima of the compounds reported here are given in Table I along with the photoluminescence lifetimes of those complexes which are also triboluminescent. All of our results are consistent with the previous assignments and are thus attributed to the $^4T_1 \rightarrow {}^6A_1$ transition. The

lifetime of $Mn(Ph_3PO)_2Br_2$ is significantly longer than those of the tetrahalo complexes. A possible explanation for the absence of photoluminescence from $Mn(Ph_3PO)_2Cl_2$ may be that its lifetime is even longer and that radiationless processes dominate its excited-state relaxation. The appreciable Stokes shift observed in the emissions ranging from 1300 cm^{-1} in $MnBr_4^{2-}$ to 2200 cm^{-1} in MnI_4^{2-} are of the order of magnitude typically observed in transition metal complexes.[12] Note that in contrast to the case of most complexes, the emitting state is expected to be distorted toward shorter metal–ligand bond distances relative to the ground state.

The triboluminescence and photoluminescence spectra of $Mn(Ph_3PO)_2Br_2$ and $(Et_4N)_2MnBr_4$ are superimposable as shown in Figures 2 and 3. For this reason, the TL is assigned to the same excited state as the photoluminescence. Superimposable TL and photoluminescence spectra are common when the emissions are long-lived, spin-forbidden phosphorescences. Only when the emitting state is very short-lived are significant differences in the TL and photoluminescence spectra found. The differences, such as those found between the TL and photoluminescence spectra of coumarin,[2] take the form of enhanced intensities on the long-wavelength side of the main peak and are attributed to the effects of the pressure on the molecule or crystal while it is emitting.

No photoluminescence could be detected from $Mn(Ph_3PO)_2Cl_2$ although TL could be detected readily and recorded. The TL spectrum is shown in Figure 4. Because the emission maximum and the band shape of the TL spectrum of this compound are very similar to those of the complexes which both photo- and triboluminesce, the TL can also be reasonably assigned to the $^4T_1 \rightarrow {}^6A_1$ phosphorescence. For organic compounds that are triboluminescent but not photoluminescent,[2] no assignments of the TL could be made because no similar compounds were available for reference. Thus $Mn(Ph_3PO)_2Cl_2$ provides the best demonstration to date of the potential use of TL as a means of determining the energies of thermally relaxed excited states in compounds from which no photoluminescence is observed. A tentative explanation for the presence of TL in the absence of photoluminescence which was offered for phthalic anhydride,[2] a pressure-induced charge transfer emitting state, is definitely not operative in the manganese complex. However, speculation about the origin of this unusual effect is probably premature.

The energies of the photoluminescences of all of the manganese complexes show an appreciable red shift as a function of increasing pressure as shown for two representative complexes in Figure 5. The decrease in the energy of the lowest energy d–d transition with increasing ligand field strength is unique to high-spin d^5 complexes. As the pressure increases, Dq increases and the crystal field stabilization energy of the excited state increases and approaches the spin-pairing energy. At large Dq values, the CFSE becomes greater than the pairing energy and the low-spin configuration becomes the ground state. Because Tanabe–Sugano diagrams for both tetrahedral and octahedral symmetries are identical for d^5 manganese(II), similar pressure effects occur for octahedral complexes. A decrease in absorption energy with increasing pressure was observed by Zahner and Drickamer in octahedral complexes of $MnCl_2$ and $MnBr_2$.[13] Our observation that the TL and atmospheric pressure photoluminescence spectra are superimposable proves that the TL emission occurs from manganese centers which are not under pressure at the time of the luminescence.

Mechanisms of the Triboluminescence. The proposed mechanisms of TL excitation which are currently under consideration may be divided into two categories: electrical and thermal population of an excited state at high pressure. Each of these mechanisms contains two subcategories which

differ in detail. Their applicability to the tetrahedral manganese(II) TL will be discussed individually in terms of our spectroscopic results.

(a) Frictional Electrification. Electrification caused by rubbing together two dissimilar materials could cause luminescence by electron impact or charge recombination. Frictional electrification of some organic systems has been measured and correlated with the energy of the highest occupied molecular orbital.[14] This mechanism may be dominant in the TL of materials excited by the action of flowing mercury.[15] However, frictional electrification has not been proven important in the triboluminescence of crystals and seems highly unlikely for the manganese system in view of the fact that TL can be produced by grinding with a wide variety of materials (steel, wood, Teflon, glass). TL can also be observed in other crystals without grinding by submersing the materials in liquid nitrogen thereby subjecting the crystals to thermal shock.[3]

(b) Piezoelectrification. Piezoelectrification could provide a second source of electrical excitation. In this mechanism, application of stress to the crystal changes the electric polarization.[16] This mechanism is expected to be very important in systems demonstrating the $^3\Pi_u \rightarrow {}^3\Pi_g$ nitrogen emission since excitation to the $^3\Pi_u$ level requires an energy of at least 88 000 cm^{-1} (about 11 eV) above the ground state.[17] It is difficult to imagine a mechanism which could allow thermal population of this state. Electron acceleration caused by a pressure-induced electronic potential difference could provide the energy to excite both the high-energy nitrogen $^3\Pi_u$ state and the lower energy Mn(II) $^4T_1$ state. The piezoelectrification mechanism would be expected to be operative only in noncentrosymmetric crystals.[16] However, tetrahedral $MX_4{}^{2-}$ complexes $((CH_3)_4N)_2MCl_4$ (M = Co, Ni, Zn, Mn) are all in a centrosymmetric *pnma* space group.[18,19]

It is not known if changing the cation from Me$_4$N$^+$ to Et$_4$N$^+$ or Ph$_3$MeP$^+$ changes the space group. No TL is observed from $(Me_4N)_2MnCl_4$[8] whose structure and space group are known to be centrosymmetric. X-ray diffraction photographs alone cannot help in determining the centricity of the space group for the various complexes since the centric *Pnma* and acentric *Pn2$_1$a* space groups both have the same systematic absences.[20] It has not been positively determined that all of the complexes are centrosymmetric, so the electrification mechanism cannot be ruled out.

(c) Thermal Population of States Coupled Differently to the Medium. If the ground state and an excited state respond differently to the medium, the application of pressure can cause a shift in the relative energies and the internuclear coordinates of their minima.[21] Thus at high pressure, thermal population of a state different from the ground state could occur even though the Franck–Condon transition energy is much larger than kT. Release of the pressure could result in molecules in their excited states at the lower pressure. Drickamer[21] has demonstrated that states which are higher in energy than the ground state at atmospheric pressure can become thermally populated at high pressures.

In order to investigate the relative changes in energy of the ground and excited states of the tetrahedral manganese(II) complexes, the photoluminescence spectra were measured at pressures of up to 42 kbars. The observed decrease in emission energy with increasing pressure is consistent with the thermal population mechanism. However, there are four additional considerations which must be included in the analysis.

First, extrapolation of the high-pressure emission data predicts that the $^4T_1$ state is within kT of the $^6T_1$ state at hydrostatic pressures ranging from 500 to 700 kbars for the triboluminescent complexes. The extrapolated values reported here assume that the relationship between the emission energy

and the applied pressure remains linear at pressures above 40 kbars. This assumption is probably not true. Curvative at higher pressures has been found for many organic systems.[22] Thus, the extrapolated values represent lower limits to the true values. On the other hand, Drickamer has shown that the Frank–Condon transition energies between two states observed spectroscopically may quite generally be much larger than the energies between the potential minima of the states.[22] The latter energy separation is the thermal energy of interest in this TL mechanism. For this reason, the extrapolated pressure at which the Frank–Condon transition energy is zero is probably an upper limit to the true pressure actually required for thermal population. Finally, the only excited state being observed in the luminescence experiment is $^4T_1$. From the Tanabe–Sugano diagrams, the $^2T_2$ state will cross the $^4T_1$ state at some intermediate pressure and become the lowest energy excited state. Thus, thermal population of the $^2T_2$ excited state will occur at a lower pressure than that required for the $^4T_1$ state. Upon release of the pressure, the $^2T_2$ state could in turn populate the $^4T_1$ state and lead to the triboluminescence.

Second, can the pressures required to thermally populate the excited states be obtained in the triboluminescence experiment? The pressures discussed above are hydrostatic pressures. The local pressures and shear pressures encountered when the crystals are fractured could be large enough at local sites to thermally populate excited states, especially if the extrapolated values of the required pressure are extreme upper limits.

Third, there is no correlation between the extrapolated pressure at which thermal population can occur and the presence or absence of TL in the manganese complexes. A higher pressure might be expected to be required to thermally populate the excited states of the nontriboluminescent complexes than that required for the triboluminescent ones. The absence of such a correlation is probably related to the mechanical properties of the crystals. A crystal with a larger shear modulus would be better able to generate high local pressures when under stress. Thus the presence or absence of TL might be more closely related to a mechanical crystal property than to the extrapolated pressure in a series of similar complexes.

Fourth, it is difficult to propose an intramolecular pressure mechanism which could explain the emission of adsorbed molecular nitrogen. Intermolecular interactions could be responsible but cannot be analyzed in the absence of detailed knowledge of the crystal sites occupied by the nitrogen.

(d) Thermal Population of a Distorted Molecule. The effect of the pressure on the crystal could cause a molecular distortion which changes the point group of the molecule. If the ground state of the undistorted molecule correlates with a high-energy state of the distorted molecule and at some degree of distortion crosses a state which correlates with an excited state of the undistorted molecule, the application of pressure will cause a distortion which in turn could populate the latter state. Because the populated state correlates with an excited state of the undistorted molecule, release of the pressure could result in an excited, undistorted molecule which would luminesce. This mechanism was discussed in detail and ultimately rejected for the TL of the uranyl ion.[23]

A D_{2d} distortion of the $MCl_4{}^{2-}$ tetrahedra in $[(CH_3)_4N]_2MCl_4$ complexes has been observed at atmospheric pressure and attributed to crystal-packing forces.[10] Application of pressure to the crystal would decrease the unit cell size, would increase the intermolecular forces, and could increase the amount of D_{2d} distortion. The extreme of this type of distortion would produce a square-planar geometry. Since it is highly improbable that the extremely distorted molecule would remain high spin, a large distortion would cause spin

pairing which would correlate with an excited state when the pressure is suddenly released. This mechanism of TL excitation by molecular distortion is attractive because the major effect of pressure on a crystal is the shortening of intermolecular distances rather than the bond distances.[22] Because the bending force constants are much lower than the stretching force constants, a geometry change is energetically more likely to occur as a result of the increased intermolecular repulsions.

The important role of the counterion dependence on the emission energy vs. pressure graphs is illustrated by $(MePh_3P)_2MnCl_4$ and $(pyH)_2MnCl_4$. The former complex contains the largest cation and shows a stronger coupling with pressure (slope -39 cm^{-1}/kbar) than the latter complex (slope -20 cm^{-1}/kbar). In addition, the latter complex displays a characteristic unique among those of all other Mn(II) complexes studied here. With increasing pressure, the luminescence spectrum develops a large band in the red region. The $^4T_1 \rightarrow {}^6A_1$ emission becomes a small shoulder on the much larger red band. The luminescence changes reversibly from green to red with pressure. Two possible origins of the red emission are (a) luminescence from a low-spin tetrahedral complex formed at high pressure and (b) luminescence from an octahedral complex formed under high pressure containing coordinated pyridine. This phenomenon is currently under further investigation.

No unambigous choice can be made between the various mechanisms on the basis of the spectral data. The observation of the high-energy emission from the absorbed molecular nitrogen strongly implicates an electrical mechanism. However, the intensity of the nitrogen emission is very weak compared to that observed in aniline hydrochloride[4] or sucrose.[5] Thus, electrification may be a minor component of the overall excitation process. Furthermore, frictional electrification does not appear to be important. Thermal population of the excited states under pressure is likely in the manganese system based on the high-pressure spectroscopic results. However, this mechanism may not be unique even in centrosymmetric cyrstals because crystal defects could provide a small number of sites where the centricity is destroyed and electrification could be important. Thus, several of the proposed mechanisms may be operating simultaneously.

Note Added in Proof. Recent x-ray structural determinations of the quinolinium and pyridinium salts of MnCl$_4^{2-}$

have found both crystals to have the centrosymmetric space group $P\bar{1}$.[24] Neither crystal is triboluminescent. To date, all of the manganese complexes with known space groups are centrosymmetric and are not triboluminescent. No generalizations can be made until the space groups of some triboluminescent crystals are known. We thank Professor R. Willett for communicating his results on the quinolinium salt to us prior to publication.

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Complexes of Alkyl and Aryl Cyanides. 9.[1] Reactions of *cis*-ReCl4(CH3CN)2 with Bidentate Phosphorus and Arsenic Donors: Cis–Trans Isomerization in Complexes of the Type ReCl4L2

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The reactions of *cis*-ReCl$_4$(CH$_3$CN)$_2$ with the ligands bis(diphenylphosphino)methane (dppm), bis(1,2-diphenylphosphino)ethane (dppe), and 1-diphenylphosphino-2-diphenylarsinoethane (arphos) lead to the formation of the six-coordinate complexes of the types *cis*-ReCl$_4$(LL), polymeric *trans*-ReCl$_4$(LL), or monomeric *trans*-ReCl$_4$(LL)$_2$, depending upon the choice of reaction conditions. The cis and trans isomers of ReCl$_4$(LL), where LL = dppe or arphos, are a novel series of complexes since these are the first geometric isomers to have been isolated in which bidentate tertiary phosphine or arsine ligands containing the ethane skeleton are either in the gauche (chelating) or trans (bridging) conformations. The factors which control the course of these reactions are discussed.

Introduction

The reduction of rhenium(V) chloride by acetonitrile to yield *cis*-tetrachlorobis(acetonitrile)rhenium(IV) was first reported

in 1968.[2] It was found that this complex reacts with a variety of monodentate donors to yield substitution products of the type *trans*-ReCl$_4$L$_2$, where L = PPh$_3$, AsPh$_3$, etc.[2] The