Correlation of Structure and Triboluminescence for Tetrahedral Manganese(II) Compounds

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To investigate the structural basis of triboluminescence, several known tetrahedrally coordinated Mn(II) complexes have been synthesized according to literature methods and their crystal structures have been determined by X-ray diffraction. Among them, $(MePh_3P)_2[MnCl_4]$ (**2**), $a = 15.4804(4)$ Å, cubic, space group $P2_13$, $Z = 4$; $(Et_4N)_2[MnBr_4]$ (**4**), $a = 13.362(1)$ Å, $c = 14.411(1)$ Å, tetragonal, space group $P\bar{4}2_1m$, $Z = 4$; $MnBr_2(OPPh_3)_2$ (**7**), $a = 9.974(1)$ Å, $b = 10.191(3)$ Å, $c = 10.538(2)$ Å, $\alpha = 65.32(1)°$, $\beta = 63.49(1)°$, $\gamma = 89.44(2)°$, triclinic, space group $P1$, $Z = 1$; and $MnBr_2(OAsPh_3)_2$ (**10**), $a = 17.816(3)$ Å, $b = 10.164(1)$ Å, $c = 18.807(3)$ Å, orthorhombic, space group $Pca2_1$, $Z = 4$ were reported to be triboluminescent and $(Me_4N)_2[MnCl_4]$ (**3**), $a = 9.016(3)$ Å, $b = 36.90(2)$ Å, $c = 15.495(3)$ Å, $\beta = 90.72(3)°$, monoclinic, space group $P2_1/n$, $Z = 12$, and $MnI_2(OAsPh_3)_2$ (**11**), $a = 10.094(4)$ Å, $b = 10.439(2)$ Å, $c = 34.852(2)$ Å, $\alpha = 83.17(4)°$, $\beta = 86.09(2)°$, $\gamma = 75.16(3)°$, triclinic, space group $P\bar{1}$, $Z = 4$, were reported to be not triboluminescent. The result supports the correlation between space group acentricity and triboluminescence activity.

Introduction

The phenomenon of triboluminescence (sometimes called mechanoluminescence) has been known for centuries,[1] but only in recent decades has progress been made in (a) understanding the conditions for its occurrence and (b) identifying the emitting species in each case. The phenomenon occurs in both organic and inorganic materials, a well-known case of the former being that of sucrose.[2] It has been well established that the emission centers are, in some cases, the gas molecules surrounding the crystals being crushed (e.g., atmospheric nitrogen in the case of sucrose) and, in other cases, one of the ions or molecules making up the crystals. There are cases in which both of these play a role.

Many conjectures have been advanced to explain how the energy necessary to create the emission is generated, but the one most generally accepted[3] is that very high local electric fields are created as the crystals fracture. If this is true, it is necessary that the crystals which fracture be noncentrosymmetric, so that opposite sides of a crack can be oppositely charged. While it is impossible to prove on purely empirical grounds that there is no such thing as a centrosymmetric crystal that triboluminesces, it is worthwhile investigating as many cases as possible to see if any genuine example can be found. Should that happen, it would mean one of two things: (1) the relationship between crystal acentricity and the creation of electric fields at fractures is not rigorous or (2) there is some other way (or ways) in which the mechanical energy of crushing crystals can be transformed into molecular excitation energy.

In 1961 and 1962, it was first reported that triboluminescence occurs in some compounds that contain tetrahedrally coordinated Mn(II)[4] but not in other chemically similar ones. No crystal structures were available at that time. Later, Zink and co-workers carried out beautiful studies that showed that the triboluminescence, when observed, was due to the manganese ions.[5] Of the

Table 1. Properties of Tetrahedral Complexes of Manganese(II)

compound[a]	TL[a]	spectrum measured[b]	space group
1, $(PyH)_2MnCl_4$	no		$P\bar{1}$[c]
2, $(Me_3PhP)_2MnCl_4$	yes	yes	$P2_13$[d]
3, $(Me_4N)_2MnCl_4$	no		$P2_1/n$[d]
4, $(Et_4N)_2MnBr_4$	yes	yes	$P\bar{4}2_1m$[d]
5, $(Bu_4N)_2MnI_4$	no		?
6, $(Ph_3PO)_2MnCl_2$	at 80 K	yes	$Fdd2$[e]
7, $(Ph_3PO)_2MnBr_2$	yes	yes	$P1$[d]
8, $(Ph_3PO)_2MnI_2$	yes	no	$P1$[f]
9, $(Ph_3AsO)_2MnCl_2$	no		$P2_1/n$[g]
10, $(Ph_3AsO)_2MnBr_2$	at 80 K	no	$Pca2_1$[d]
11, $(Ph_3AsO)_2MnI_2$	no		$P\bar{1}$[d]

[a] Reference 5 for **1**−**5**; ref 4a for **6**−**11**. [b] Reference 4. [c] Brassy, C.; Robert, R.; Bachet, B.; Chevalier, R. *Acta Crystallogr.* **1976**, *B32*, 1371. [d] This work. [e] Tomita, K. *Acta Crystallogr.* **1985**, *C41*,1832. [f] Beagley, B.; McAuliffe, C. A.; Pritchard, R. G.; White, E. W. *Acta Chem. Scand.* **1988**, *A42*, 544. [g] Oraib, E.-S.; Godfrey, S. M.; McAuliffe, C. A.; Matear, P. P.; Pritchard, R. G. *Inorg. Chim. Acta* **1993**, *209*, 41.

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Table 2. Crystallographic Data for $(MePh_3P)_2[MnCl_4]$ (**2**), $(Me_4N)_2[MnCl_4]$ (**3**), $(Et_4N)_2[MnBr_4]$ (**4**), $MnBr_2(OPPh_3)_2$ (**7**), $MnBr_2(OAsPh_3)_2$ (**10**), and $MnI_2(OAsPh_3)_2$ (**11**)

	compound					
	2	**3**	**4**	**7**	**10**	**11**
formula	$C_{38}H_{36}Cl_4MnP_2$	$C_8H_{24}Cl_4MnN_2$	$C_{16}H_{40}Br_4MnN_2$	$C_{36}H_{30}Br_2MnO_2P_2$	$C_{36}H_{30}As_2Br_2MnO$	$C_{36}H_{30}As_2I_2MnO_2$
fw	751.35	345.03	635.08	771.30	859.20	953.18
cryst syst	cubic	monoclinic	tetragonal	triclinic	orthorhombic	triclinic
space group	$P2_13$	$P2_1/n$	$P\bar{4}2_1m$	$P1$	$Pca2_1$	$P\bar{1}$
a (Å)	15.4804(4)	9.016(3)	13.362(1)	9.974(1)	17.816(3)	10.094(4)
b (Å)	15.4804(4)	36.90(2)	13.362(1)	10.191(3)	10.164(1)	10.439(2)
c (Å)	15.4804(4)	15.495(3)	14.411(1)	10.538(2)	18.807(3)	34.852(2)
α (deg)	90	90	90	65.32(1)	90	83.17(4)
β (deg)	90	90.72(3)	90	63.49(1)	90	86.09(2)
γ (deg)	90	90	90	89.44(2)	90	75.16(3)
V (Å^3)	3709.8(2)	5155(4)	2573.0(3)	850.1(3)	3405.6(8)	3522(2)
Z	4	12	4	1	4	4
ρ (g cm^{-3})	1.345	1.334	1.639	1.507	1.676	1.798
μ (mm^{-1})	0.756	1.368	6.727	2.863	4.693	4.022
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	213(2)	213(2)	293(2)	213(2)	213(2)	213(2)
R_1,[a] wR$_2$[b] [$I > 2\sigma(I)$]	0.034, 0.088	0.057, 0.142	0.041, 0.096	0.037, 0.097	0.060, 0.144	0.049, 0.108
R_1,[a] wR$_2$[b] (all data)	0.037, 0.097	0.070, 0.159	0.105, 0.122	0.038, 0.099	0.072, 0.160	0.060, 0.118
GOF[c]	1.101	1.123	1.019	1.044	1.097	1.100
Flack parameter	0.19(3)		0.14(3)	−0.02(1)	−0.02(3)	

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})]^{1/2}$, based on all data.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(MePh_3P)_2[MnCl_4]$ (**2**), $(Me_4N)_2[MnCl_4]$ (**3**), $(Et_4N)_2[MnBr_4]$ (**4**), $MnBr_2(OPPh_3)_2$ (**7**), $MnBr_2(OAsPh_3)_2$ (**10**), and $MnI_2(OAsPh_3)_2$ (**11**)

		2	
Mn(1)−Cl(1)	2.352(1)	Cl(1)−Mn(1)−Cl(2A)	108.76(2)
Mn(1)−Cl(2)	2.378(7)	Cl(2)−Mn(1)−Cl(2A)	110.17(2)
		3	
Mn(1)−Cl(1)	2.374(2)	Cl(1)−Mn(1)−Cl(2)	110.38(9)
Mn(1)−Cl(2)	2.347(2)	Cl(1)−Mn(1)−Cl(3)	108.55(8)
Mn(1)−Cl(3)	2.351(2)	Cl(2)−Mn(1)−Cl(3)	109.12(8)
Mn(1)−Cl(4)	2.372(2)	Cl(2)−Mn(1)−Cl(4)	108.56(9)
		Cl(3)−Mn(1)−Cl(4)	111.14(9)
		Cl(4)−Mn(1)−Cl(1)	109.09(9)
		4	
Mn(1)−Br(1)	2.504(2)	Br(1)−Mn(1)−Br(2)	108.59(5)
Mn(1)−Br(2)	2.498(1)	Br(1)−Mn(1)−Br(3)	111.75(8)
Mn(1)−Br(3)	2.496(2)	Br(2)−Mn(1)−Br(3)	107.89(5)
		7	
Mn(1)−O(1)	2.036(5)	O(1)−Mn(1)−O(2)	101.7(2)
Mn(1)−O(2)	2.027(5)	O(1)−Mn(1)−Br(1)	109.8(2)
Mn(1)−Br(1)	2.467(1)	O(1)−Mn(1)−Br(2)	114.2(2)
Mn(1)−Br(2)	2.475(1)	O(2)−Mn(1)−Br(2)	103.7(2)
		O(2)−Mn(1)−Br(1)	111.6(2)
		Br(1)−Mn(1)−Br(2)	114.95(5)
		10	
Mn(1)−O(1)	2.02(1)	O(1)−Mn(1)−Br(1)	110.8(3)
Mn(1)−O(2)	2.00(1)	O(1)−Mn(1)−Br(2)	110.0(3)
Mn(1)−Br(1)	2.498(3)	O(1)−Mn(1)−O(2)	100.5(4)
Mn(1)−Br(2)	2.480(3)	O(2)−Mn(1)−Br(2)	115.1(3)
		O(2)−Mn(1)−Br(1)	106.7(3)
		Br(1)−Mn(1)−Br(2)	112.9(1)
		11	
Mn(1)−O(1)	2.008(6)	O(2)−Mn(1)−O(1)	101.8(2)
Mn(1)−O(2)	2.005(6)	O(2)−Mn(1)−I(1)	109.2(2)
Mn(1)−I(1)	2.684(2)	O(1)−Mn(1)−I(1)	111.1(2)
Mn(1)−I(2)	2.720(2)	O(2)−Mn(1)−I(2)	110.8(2)
		O(1)−Mn(1)−I(2)	108.5(2)
		I(1)−Mn(1)−I(2)	114.73(6)

Table 4. Calculation of Covalent Bond Radius of Mn (Covalent Radii for Cl, Br, I: 0.99, 1.14, 1.33 Å, Respectively[7])

compound	bond type	d_{Mn-X} (exp, Å)	radius of Mn (Å)
1	Mn−Cl	2.365(2)	1.38
2	Mn−Cl	2.3712(8)	1.38
3	Mn−Cl	2.361(2)	1.37
4	Mn−Br	2.499(2)	1.36
6	Mn−Cl	2.293(1)	1.30
7	Mn−Br	2.471(1)	1.33
8	Mn−I	2.667(1)	1.34
9	Mn−Cl	2.344(1)	1.35
10	Mn−Br	2.489(3)	1.35
11	Mn−I	2.702(2)	1.37

11 compounds reported, all listed in Table 1, only four have heretofore been crystallographically characterized, namely, **1**, **6**, **8**, and **9**. References for these are given in the footnotes to the table. We felt that this set of compounds provided an excellent opportunity to explore the hypothesis that acentricity is necessary for triboluminescence, and we have proceeded to determine the crystal structures for all but one of the remaining seven compounds. We have also redetermined the structure of **6**.

Experimental Section

All of the compounds were prepared by the methods previously described.[4] Good quality crystals were obtained with no particular difficulty except in the case of **5**, which tends to form clusters of very thin plates. Since this one is not triboluminescent, we have not pursued its structure further.

Crystal Structure Determinations. Crystals of **2** were obtained directly during the cooling process. Crystals of **3** were obtained by the vapor phase diffusion of ether into a methanol solution. Single crystals of **4**, **6**, **7**, **10**, and **11** were obtained by the vapor phase diffusion of ether into ethanol solutions. All crystal data except those for **4** were measured at 213 K on a Nonius FAST diffractometer. Data for **4** were measured at 293 K on a Nonius CAD4 diffractometer. All structures were solved by direct methods and refined using SHELXL-93. In every case, the space group determination was straightforward, although we were careful to test the possibility that the noncentrosymmetric structures might be centrosymmetric. Intensity statistics strongly indicated that each of these is noncentrosymmetric, but this indication is not always reliable for metal-containing structures. For **2**, $P2_13$ is uniquely defined in Laue group $m3$. For **4**, an alternate space group is $P42_12$ (also noncentrosymmetric), but the structure is incompatible with the additional symmetry (4-fold and 222 site symmetry). Compound **7** is in space group $P1$ with $Z = 1$, for which there is no alternative. For **10**, an alternate space group is $Pbcm$, which is completely incompatible with the structure due to the additional symmetry elements (mirror,

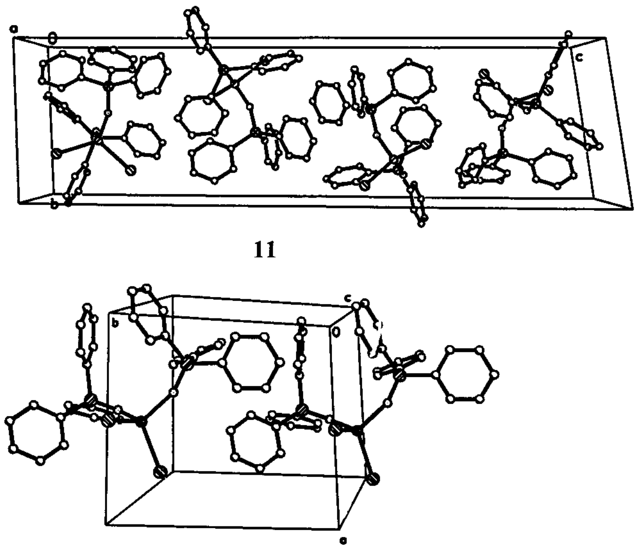

Figure 1. Packing diagrams of $(Ph_3AsO)_2MnI_2$ (**11**) and $(Ph_3PO)_2MnI_2$ (**8**).

2-fold, and inversion centers). The behavior of the Flack parameters[6] was followed for each of these structures and converged to a value near zero in each case. The original model for **4** gave a Flack parameter near 1.0, and the coordinates were inverted to produce the correct absolute structure. The NEt_4 groups in **4** were highly disordered. All hydrogen atoms were treated as riding on the corresponding carbon atoms. More detailed crystallographic data are listed in Table 2. Selected bond lengths and angles for the six structures are listed in Table 3, and obviously they vary within the normal range.

Discussion

As a result of this work, one can conclude that for the tetrahedral complexes that have been examined, 11 in all, only those six that form noncentric crystals are triboluminescent. Conversely, it can be said (with the exception of **5**, where the crystal structure is still undetermined) that no centric crystals of tetrahedral manganese(II) have displayed triboluminescence. Thus, for this class of compounds, the general picture that triboluminescence arises when electric fields are created at the interfaces of cracks is supported.

We have sufficient redundant data to estimate reliably the radius of the Mn^{II} atom as it occurs in its tetrahedral complexes (Table 4). This was done by subtracting the covalent radii of the three halogen atoms, Cl, Br and I, as given by Pauling.[7] The average over all the structures is 1.35 Å, but with the removal of the particularly deviant value from **6** an average value of 1.36 Å is obtained. Because the reported value for **6** was so deviant, we redetermined this structure. We found that the reported structure is correct, but we have obtained slightly more accurate results.

The crystal structures of the six $(Ph_3EO)_2MnX_2$ compounds, **6**−**11**, present some interesting comparisons. We may first note that none of the $(Ph_3AsO)_2MnX_2$ compounds, **9**−**11**, are isomorphous to their $(Ph_3PO)_2MnX_2$ analogues, nor to one another. Two of the $(Ph_3PO)_2MnX_2$ compounds, those with X = Br and I, are isomorphous, but the chloro compound crystallizes differently. It is interesting that the two $(Ph_3EO)_2MnI_2$ compounds crystallize in $P1$ ($Z = 1$ for E = P) and $P\bar{1}$ ($Z = 4$ for E = As). However, the molecular packing is quite different in the two cases, as shown in Figure 1.

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Supporting Information Available: X-ray crystallographic files, in CIF format, containing data for structures **2**, **3**, **4**, **7**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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