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Infrared studies of lead(II) halide-1,10-phenanthroline photosensitive materials

Alicia Glatfelter[a], Cecil Dybowski[a], Shi Bai[a], David Kragten[a],
Margaret J. Blake[b], Santiago Segarra[b], Dale L. Perry[b,*]

[a] *Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA*
[b] *Lawrence Berkeley National Laboratory, Mail Stop 70A-1150, Berkeley, CA 94720, USA*

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ABSTRACT

Infrared spectroscopic studies of 1:1 and 1:2 complexes of lead(II) bromide and lead(II) iodide with 1,10-phenanthroline were reported. Vibrational assignments are made by comparison to reported spectra of the uncomplexed 1,10-phenanthroline molecule. Small shifts of the ligand vibrational bands are characteristic of the complexes.

1. Introduction

Metal ion aromatic hydrocarbon complex-based materials containing organic ligands such as 1,10-phenanthroline have found extensive use in a wide range of applications. The crystal structure and thermal properties of rare earth-1,10-phenanthroline materials have been studied [1], while ionization isomers of cobalt and nickel have been reported [2]. The effects of redox-active groups in platinum(II) compounds have been studied [3], and biological complexes of ruthenium(II)- and vanadium-based compounds [4,5] have been investigated. Other systems that make use of 1,10-phenanthroline are electro-polymerized films on electrode surfaces [6] and 1,10-phenanthroline-derived polymers [7].

Lead(II) salts also have been found to possess physical, electronic, and structural properties that are amenable to a wide number of different applications. Structural aspects of $Pb(NO_3)_2$ complexes of 1,10-phenanthroline, for example, have been investigated by X-ray crystallography [8], as have one-dimensional polymers [9]. They have been used as solution complexing species for the analysis of cadmium [10].

Vibrational studies of organic polymers and related materials such as complexes with metal ions have been conducted by many groups [11–13]. Infrared investigations have focused on Re(I) materials complexed with 1,10-phenanthroline [14], lead(II) polymers of acetate–saccharinates [15], and Cu(II) complexes of the mixed 1,10-phenanthroline-substituted lactate system [16]. The present work reports an infrared study of high-purity, X-ray crystallographic-quality crystals of the photoactive materials $PbBr_2(1,10\text{-phenanthroline})_x$ and $PbI_2(1,10\text{-phenanthroline})_x$ having both 1:1 and 1:2 molecular ratios of lead(II) halide:1,10-phenanthroline molecules. The spectra are discussed with respect to the X-ray crystallographically determined structures of the materials.

2. Experimental

2.1. Synthesis

Both the 1:1 and 1:2 adduct materials were synthesized as previously described [17], with the 1:1 materials using equimolar amounts of either $PbBr_2$ or PbI_2 and 1,10-phenanthroline in ethanol in the sidearm diffusion technique. The 1:2 materials of 1,10-phenanthroline with $PbBr_2$ and PbI_2 were prepared from a suspension of the lead(II) halide in ethanol with stirring using an eightfold excess of 1,10-phenanthroline in ethanol slowly added at room temperature. The product was obtained by filtration, washing with ethanol, and drying under vacuum. The reaction mixtures for both the 1:1 and 1:2 syntheses were shielded from light.

2.2. Infrared spectra

All FTIR spectra were obtained using a Nicolet Magna-IR 860 spectrometer equipped with an MCT detector. The spectra were collected in absorption mode from 600 to 4000 cm^{-1}. Measurements

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[*] Corresponding author. Tel.: +1 510 486 4819; fax: +1 510 486 5799.
E-mail address: dlperry@lbl.gov (D.L. Perry).

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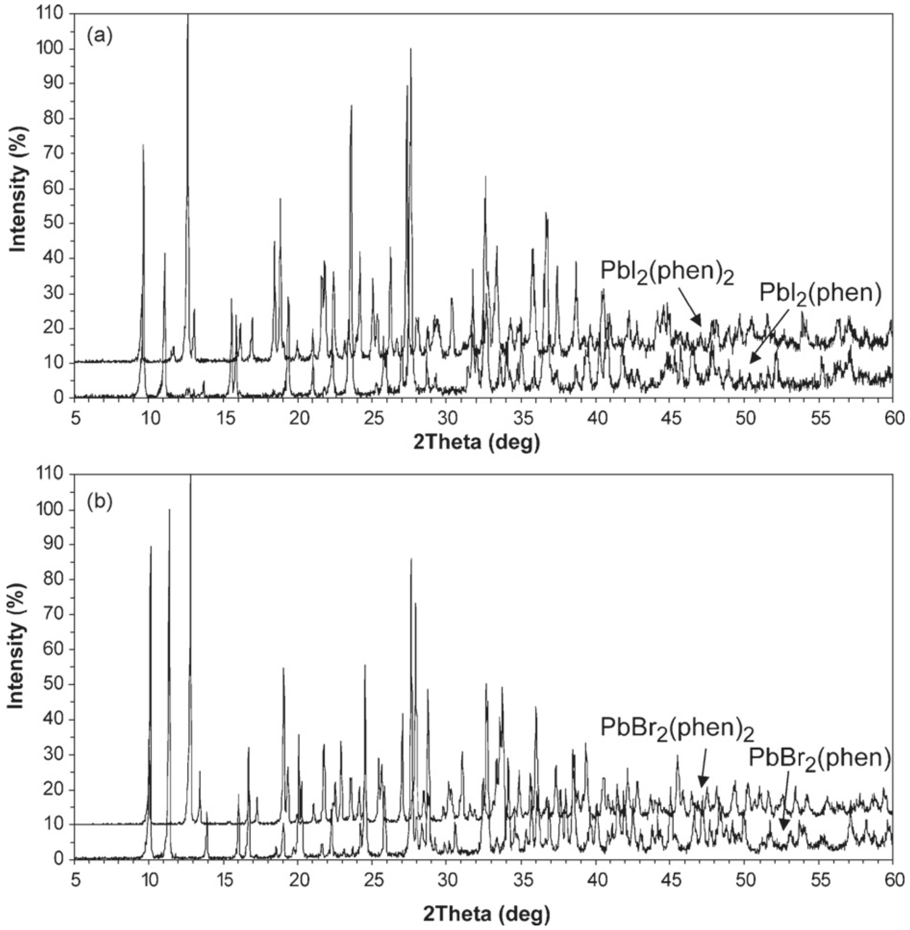

Fig. 1. (a) and (b) X-ray diffractograms of PbX_2(phenanthroline) and PbX_2(phenanthroline)$_2$.

were performed at room temperature under a flow of nitrogen. The compounds were pressed into pellets with dry FTIR-grade KBr.

2.3. X-ray diffraction patterns

Powder X-ray diffraction studies of the materials were performed with a Philips X'Pert X-ray diffractometer, Model PW3040 MPD, using the Cu Kα line at 1.54056 Å. Scattering was measured from $2\theta = 4^\circ$ to 60° at intervals of 0.02°. The X-ray powder patterns and strongest *d*-spacings for the complexes are given in Fig. 1 and Table 1, respectively.

3. Results and discussion

A full vibrational assignment of the 1,10-phenanthroline molecule has been published by several groups [18–20]. Assignments are based on several techniques: a combination of symmetry analyses, especially by comparing infrared spectra with Raman spectra and by polarization measurements, isotopic labeling, and normal mode analysis using force field calculations. Most of the published spectra were recorded as mulls with Nujol or hexachlorobutadiene. It is noteworthy that the vibrational frequencies for this molecule have a close resemblance with those of benzene and of pyridine, the two aromatic molecules that make up the aromatic system of 1,10-phenanthroline [21a,b]. The assignments are given in Table 2.

Table 1
Two strongest *d*-spacings in the powder X-ray diffractograms of the 1:1 and 1:2 materials of PbX_2 with 1,10-phenanthroline

Material	d_1 (Å)	d_2 (Å)
PbI_2(phenanthroline)	9.1106	7.9645
PbI_2(phenanthroline)$_2$	9.2631	6.9974
$PbBr_2$(phenanthroline)	8.7163	7.7420
$PbBr_2$(phenanthroline)$_2$	8.8028	6.8995

In the range over which the IR spectra were recorded, only the 1,10-phenanthroline ligand gives rise to bands for the lead adducts. The lead–1,10-phenanthroline bond stretch is predicted to be at much lower wave numbers [22,23].

Upon complexation of 1,10-phenanthroline with a lead(II) halide, a number of changes in the vibrational spectrum are expected. First, bonding with the metal ion affects the intraligand bonding. In particular, vibrations involving the ligating nitrogen atoms are affected. The magnitude of the shift depends on the bond strength. Second, it is possible that factor group band splitting arises in the crystal [24], due to the presence of a crystal field. Another possible effect may be the variation in phase of vibration of the different complexes in the unit cell. Because of these effects, some or all of the vibrational degeneracies of the free molecule may be lifted in the crystal. Of course, the magnitudes of the frequency splittings depend upon the strength of the crystal field and of the interactions between the complexes.

In Table 2 the vibrational frequencies are tabulated, as measured in our laboratory, for the 1:1 and the 1:2 adducts of PbI_2 and $PbBr_2$ with 1,10-phenanthroline. When comparing the frequencies with

Table 2
Assignments of IR-active vibrational bands (in cm^{-1}) of 1,10-phenanthroline (phen), $PbX_2(phen)$, and $PbX_2(phen)_2$, where X = Br, I, in KBr

1,10-Phenanthroline			$PbI_2(phen)_x$		$PbBr_2(phen)_x$	
			1:1	1:2	1:1	1:2
Mode	Literature [1]	This work	This work	This work	This work	This work
26 (B_2)	624 (m)	623 (m)	637 (m)	634 (m)	638 (m)	634 (m)
4 (A_1)	708 (wm)	706 (w)				
27 (B_2)	724 (m)	724 (w)	722 (s)	719 (m) + 725 (s)	722 (s)	719 (s) + 725 (s)
51 (B_1)	738 (vs)	739 (s)			739 (w)	
50 (B_1)	779 (m)	778 (w)	781 (m)	771 (m)	786 (m)	770 (m)
60 (A_2)	810 (w)	814 (w)	806 (w)		809 (vw)	804 (w)
49 (B_1)	840 (s)	840 (ssh)	828 (wsh) + 853 (m)	846 (s)	830 (wsh)	846 (s)
5 (A_1)	853 (vs)	855 (s)	860 (m)	859 (m)	858 (s)	859 (m)
28 (B_2)	896 (vvw)	882 (w)	894 (w)	892 (w)	895 (w)	894 (w)
57 (A_2)	956 (w)	956 (w)	958 (vw)	957 (w)		960 (w)
46 (B_1)	969 (w)	969 (w)		968 (w)	963 (vw)	972 (w)
29 (B_2)	988 (m)	987 (m)	982 (vw)	989 (wsh)	985 (vw)	993 (wsh)
Comb. band	997 (w)	995 (w)	994 (vw)	994 (w)	999 (vw)	998 (w)
6 (A_1)	1037 (m)	1036 (w)	1031 (vw)	1037 (vw)	1032 (vw)	
30 (B_2)	1079 (m)	1079 (w)	1086 (w)	1087 (wsh)	1086 (w)	1089 (wsh)
7 (A_1)	1092 (s)	1091 (m)	1098 (s)	1096 (m)	1100 (m)	1096 (m)
31 (B_2)	1137 (m)	1138 (m)	1143 (s)	1141 (w)	1146 (m)	1139 (w)
9 (A_1)	1186 (vw)	1185 (w)		1188 (vw)	1197 (vwsh)	1188 (vw)
33 (B_2)	1207 (wsh)	1207 (wsh)	1205 (w)	1205 (w)	1207 (w)	1206 (w)
10 (A_1)	1212 (wm)	1216 (m)	1221 (w)	1221 (m)	1224 (w)	1223 (w)
12 (A_1)	1295 (w)	1295 (w)	1299 (w)	1300 (w)	1301 (w)	1302 (w)
35 ($B_{2)}$	1312 (vw)	1312 (w)	1313 (w)	1313 (w)	1315 (vw)	1314 (w)
13 (A_1)	1345 (ms)	1345 (m)	1344 (m)	1340 (m)	1346 (m)	1341 (m)
36 ($B_{2)}$	1405 (m)	1406 (w)	1412 (m)	1415 (m)	1414 (m)	1416 (m)
37 (B_2)	1422 (s)	1422 (s)	1425 (s)	1423 (s)	1426 (ms)	1424 (ms)
15 (A_1)	1446 (s)	1447 (w)	1449 (vw)	1445 (w)	1450 (vw)	1447 (vw)
38 (B_2)	1492 (m)	1492 (w)	1494 (m)	1492 (m)	1496 (m)	1492 (m)
16 (A_1)	1502 (s)	1503 (m)	1514 (s)	1512 (s)	1516 (ms)	1512 (ms)
39 (B_2)	1561 (m)	1562 (m)	1571 (m)	1569 (m)	1573 (m)	1570 (m)
40 (B_2)	1585 (ms)	1586 (m)	1586 (m)	1586 (m)	1586 (m)	1587 (m)
17 (A_1)	1597 (vw)	1598 (vw)	1600 (w)	1601 (vw)	1600 (vw)	1602 (vw)
18 (A1)	1615 (m)	1616 (w)	1619 (m)	1621 (m)	1621 (m)	1622 (m)
Comb. band	1708 (vw)	1714 (w)	1708 (vw)	1717 (vw)		
Comb. band	1763 (vw)	1764 (w)	1762 (vw) + 1773 (vw)	1764 (vw)	1771 (vw)	
Comb. band	1831 (w)	1832 (w)	1833 (vw)	1815 (w)		
Comb. band	1937 (w)	1939 (w)	1938 (vw)	1931 (vw)		
Comb. band	1964 (w)	1967 (w)	1950 (vw) + 1959 (vw)	1961 (vw)	1959 (vw) + 1966 (vw)	
Comb. band		1980 (w)	1975 (vw) + 1986 (vw)	1984 (w)	1983 (vw)	
Comb. band	2991 (wm)	2994 (w)	2988(w)	2991 (m)	2900 (w)	2985 + 2992 (m)
41 (B_2)	3008 (wm)	3010 (w)	3005 (m) + 3021 (m)	3007 (m)	3006 (w)	3008 (wm)
19 (A_1); 42 (B_2)	3032 (m)	3032 (m)	3044 (s)	3038 (s)	3024 (w)	3034 (m) + 3040 (m)
21 (A_1); 43 (B_2)	3059 (s)	3060 (m)	3060 (m)	3063 (m)	3058 (wsh)	3065 (w)
22 (A_1)	3068 (ssh)	3069 (msh)				
23 (A_1)	3082 (m)	3082 (m)	3083 (w)		3084 (vw)	

s = strong; m = medium; w = weak; v = very; sh = shoulder; br = broad. [1] Assignments for 1,10-phenanthroline are given in Refs. [18,19,20].

those of the 1,10-phenanthroline molecule, shifts – though small – are apparent for most bands. This indicates that the ligand is, indeed, forming bonds to the lead(II) ion, a fact corroborated by the single-crystal X-ray crystallography discussed below.

Comparison of the spectra of the various adducts reveals important differences. The spectra are largely similar, especially for bands at higher wave numbers. However, in the range of the aromatic C–H asymmetric deformations in the 600–900 cm^{-1} region, several bands show significant differences. These differences are shown in Fig. 2. For the 26(B_2) and 50(B_1) modes, the 1:1 adducts are shifted to higher wave numbers with respect to the 1:2 adducts by 4 and 10–16 cm^{-1}, respectively. The bromide ion causes a slightly larger shift of the 50(B_1) mode than the iodide ion. A more pronounced effect is seen for the 27(B_2) and 49(B_1) modes, arising from C–H bending vibrations of the N-containing rings and the central aromatic ring, respectively. The 1:1 adducts give rise to a singlet 27(B_2) mode, independent of the halide ion. However, for the 1:2 adducts, a doublet is observed with peaks at 719 and 725 cm^{-1}. The bromide ion gives rise to two equally strong peaks. On the other hand, the iodide ion gives rise to a medium peak at 719 cm^{-1} and a strong peak

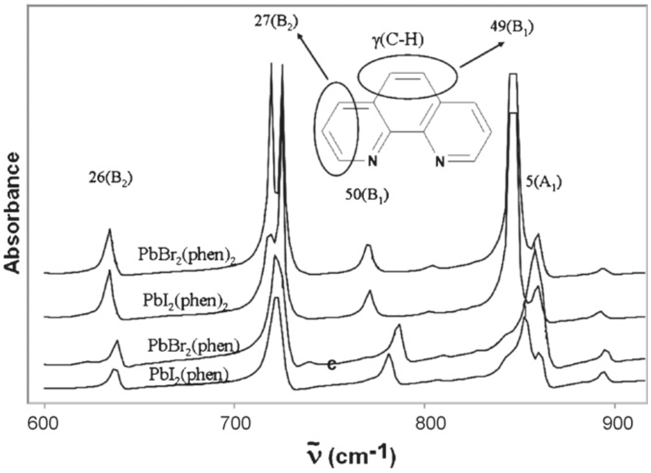

Fig. 2. Comparison of IR spectra of PbX_2(phenanthroline) and PbX_2(phenanthroline)$_2$.

at 725 cm^{-1}. For the 49(B_1) mode, a similar pattern is observed. The 1:2 adducts give rise to one strong peak at 846 cm^{-1}. The iodide 1:1 adduct gives rise to a doublet with a weak band at 828 cm^{-1} and a medium band at 853 cm^{-1}. The bromide 1:1 adduct shows only a very weak band at 830 cm^{-1}; the band at 853 cm^{-1} could be masked by the relatively strong 5(A_1) band at 858 cm^{-1}.

The differences observed in the patterns of the 27(B_2) and 49(B_1) modes are caused by differences in the crystal structures. Degeneracy of these modes is due to factor group band splitting, described above. The crystal structure of the 1:1 adduct of PbI_2 with 1,10-phenanthroline, as published by several workers [25,27], shows a one-dimensional polymeric structure whereby the aromatic ligands are stacked. For the 1:1 adduct, two iodide ions are binding *trans* to the phenanthroline and occupy axial positions in roughly octahedral coordination [7,8]. The Pb–I bond lengths are 3.323 and 3.197 Å, corresponding to weak and intermediate bond strengths, respectively [16]. The axial iodides form the backbone of the polymer chain. The *cis* I–Pb–I bond angles in the 1:1 adduct are somewhat distorted from the ideal 90°. The variations both in the bond lengths and in the bond angles may be indicative of some stereochemical activity. However, these observations may be due solely to the restrictions imposed on the structure by the formation of polymer chains and by the enforced bite angle of the phenanthroline ligand, which changes little from complex to complex, regardless of supposed stereochemical activity. Additionally, the largest *cis* angle in the coordination sphere is 109.6°, which, while significantly distorted from octahedral, is not nearly as large as *cis* angles in compounds with more clear-cut stereochemical activity, which are typically at least 125°. It is likely that the stereochemical activity of the lone pair is minimal in the 1:1 adduct.

Conversely, the single-crystal X-ray crystallographic structures of the 1:2 adducts determined in this laboratory [26], do not suggest strong intermolecular interactions leading to the formation of polymeric chains. Rather, the 1,10-phenanthroline ligands of adjacent molecules overlap, giving a herringbone structure in the long range. From the single crystal X-ray crystallographic data, it appears that the PbI_2 and $PbBr_2$ 1:2 adducts with 1,10-phenanthroline are isostructural. As already indicated by the powder diffraction spectra, the identity of the halogen present does not greatly affect the crystal structure or the coordination environment around the lead atom. However, it is clear that the structures are very different from those of the 1:1 adducts. The 1:2 adducts do not form the linear polymeric structure observed for all 1:1 adducts of lead(II) halides with 1,10-phenanthroline. Instead, the 1:2 adducts form distinctly separate molecules. The only possible long-range intermolecular bonding interactions may be hydrogen bonding between one of the hydrogen atoms of the 1,10-phenanthroline with a nearby halide ion. The lead(II) ion has a distorted octahedral coordination with two *cis*-halide ions and two bidentate 1,10-phenanthroline ligands.

Comparing the crystal structures of $PbI_2(phenanthroline)_2$ and $PbBr_2(phenanthroline)_2$ reveals only slight differences. The 1,10-phenanthroline structure and orientations are not strongly affected by the kind of halide: not only is the relative orientation of the two 1,10-phenanthroline ligands essentially identical in the iodide and bromide complexes, but also the 1,10-phenanthroline bite angles and the lead–nitrogen bond lengths are essentially the same. The greatest difference between the two structures is the lead–halide bond length: this is 3.106 Å for Pb–Br and 3.338 Å for Pb–I. Of course, this is due to the larger size of the iodide ion with respect to the bromide ion. It is remarkable that the bond angles between the two halogen ions that coordinate the lead ion and between the halogen ions and the 1,10-phenanthroline ligands are virtually unaffected by the nature of the halogen in the molecule.

For the 1:2 adduct of 1,10-phenanthroline with PbI_2, the coordination environment of the lead differs significantly from that of the 1:1 adduct. The 1,10-phenanthroline ligands form a propeller-like structure; while the iodide ligands are located *cis* to one another and are perpendicular to the plane that approximately bisects the 1,10-phenanthroline molecules and contains the lead(II) ion. The Pb-I bond length is 3.338 Å, which is slightly longer than that found for the 1:1 adduct; in addition, the I–Pb–I angle of 126.1° is significantly larger than the largest *cis* angle in the 1:1 adduct. The 1,10-phenanthroline ligands do not lie in a plane, but are staggered to minimize steric repulsions, while preserving the twofold rotational symmetry. There is one shorter and one longer Pb–N bond in each ligand, corresponding to shorter and longer bond angles between that nitrogen and the iodine located approximately *cis* to that ring. In summary, a large distortion from octahedral coordination is observed. This indicates a much more pronounced stereochemical effect than is seen for the 1:1 adduct. The lengthening of the lead–halogen bonds and the increase in the halogen–lead–halogen angle point to the lone pair being located between the two iodide ions and along the rotational axis. These indications of stereochemical activity are also observed in $PbBr_2(phenanthroline)_2$.

4. Conclusion

The FTIR spectra of 1:1 and 1:2 adducts of 1,10-phenanthroline with $PbBr_2$ and PbI_2 show subtle but distinct differences, most apparent in the 600–900 cm^{-1} region. These differences make possible the unique determination of the compound according to the stoichiometric ratio of ligand to lead(II) halide, as well as the identity of the halogen counteranion.

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