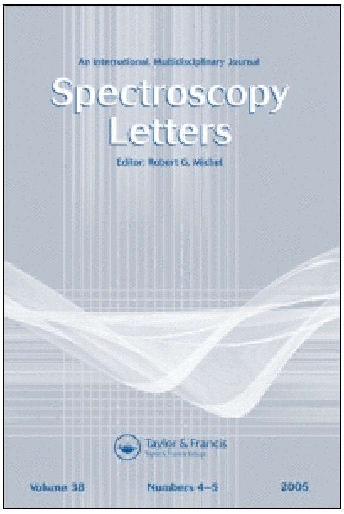

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INFRARED AND RAMAN SPECTRA OF BIS-THIOUREA LEAD(II) CHLORIDE

Key words: Environmental materials, heavy metals, lead, vibrational spectra, bis-thiourea lead chloride, low temperature spectra

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ABSTRACT

$PbCl_2.2[(SC(NH_2)_2]$ is an important complex for environmental chemistry. Single crystals were studied using infrared absorption, and Raman spectroscopy in low temperature conditions (10 K). Assignments of the lead complex bands were

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made by searching correlations and group frequencies with separate $PbCl_2$ and thiourea spectra in the solid state. Lattice modes separation was achieved down to 20 cm^{-1} in Raman and down to 50 cm^{-1} with far infrared spectroscopy. Spectral signatures of the unusual seven-coordinated lead in the complex were tentatively determined and are in accordance with structural data.

INTRODUCTION

The bis-thiourea lead(II) chloride complex $PbCl_2.2[(SC(NH_2)_2]$ is studied for environmental hazards. Lead is the final element of uranium decay and other actinides and urban gas pollutants carry lead particules in the atmosphere returning to the soil with rain water. For these reasons groundwater contamination with lead and nuclear-related environmental waste is a relevant issue in the USA. Since Cl^- is the most common anion in groundwater (the most common cation being Na^+), lead chloride can be formed and subsequently complexed with thiourea. What is needed in all cases of heavy metal complexes of thiourea (e.g. lead complex) is a rigorous, experimental data base involving the characterization of the complexes, especially spectroscopic characterization that can be used to both analyze for the species and to provide for the monitoring of the changes of the species in chemical reaction schemes that are designed for their removal from environment. Besides, another interest for this compound lies in the unusual coordination of lead. It is believed that Raman and infrared vibrational spectroscopies may bring out crucial information not only concerning the identification of metal complexes of thiourea but also about their intimate structure. In this paper we present an original contribution the vibrational study at low-temperature (10K) of this compound which is of great relevance for environmental studies.

EXPERIMENTAL

Raman spectra were recorded with a Jobin-Yvon Raman HG2S triple monochromator with holographic gratings for low temperature measurements. Further studies to characterize the crystals were carried out using a multichannel spectrometer with a charge-coupled device detector and a Bruker Fourier-transform (FT) Raman bench equipped with a specially designed x100 microscope objective. Transmission Fourier-transform infrared (FTIR, IR) spectra were obtained on

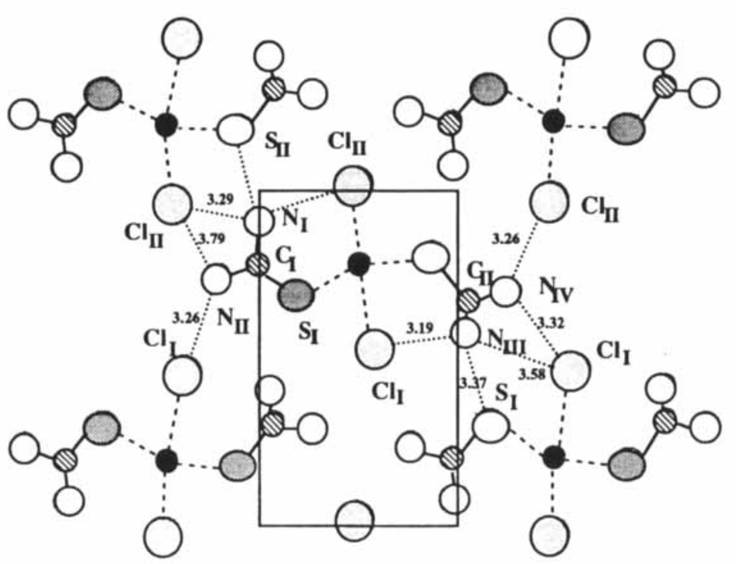

FIG. 1. Structure of $PbCl_2.2[(SC(NH_2)_2]$ with some interatomic distances. After Nardelli and Fava.[1]

20SXC and 20F Nicolet benches with materials ground in KBr or in polyethylene spectral grade powder. Crystals of the complex consisted in long transparent needles of about 10x1x0.5 mm^3 in size. Reference spectra of thiourea and $PbCl_2$ were taken on single crystals and powder samples respectively. Low temperature experiments were made in a flowing He cryostat. They were designed to ameliorate the spectral resolution of Raman lines and to avoid laser heating.

RESULTS AND DISCUSSION

Structure of $PbCl_2.2[(SC(NH_2)_2]$

The crystal structure of the complex is $Pna2_1$.[1] The coordination sphere of Pb is unusual since it includes seven atoms: four S atoms and three Cl atoms (Fig. 1).

Vibrational lines of the IR and Raman spectra.

To help the interpretation of the spectra we have analyzed separately thiourea and $PbCl_2$ in the solid state in order to seek coincidental features. Most of

TABLE 1: Vibrational frequencies of separate constituents $PbCl_2$ and thiourea (cm^{-1}). w: weak, br; broad, m: medium, s: strong, cl: cluster (the band are not well resolved).

Raman 10 K	IR (Room temperature)
$PbCl_2$	
29(m), 34(w), 42(vs), 52(w), 57(w), 64(m), 90(w), 95(w), 108(w), 129(w), 133(w), 138(w), 150(br, m), 162(br, s), 184(w), 218(w), 241(w)	106(s,cl), 120(s, cl), 180(s, cl), 215(s, cl), 338(m), 588(m, cl), 665 (m), 1035(m, br), 1192 (w), 1393(vs), 1519(m), 1622(w)
Thiourea	
54(w), 69(s), 91(w), 105(s), 116(s), 125(w), 134(s), fluorescent background (fb), 481(s), 491(w), 520(vw), 600,(vw) 734(s), 1098(s), 1386(s), fb, 3173(s), 3200(w), 3289(w), 3349(m), 3391(m)	67(m, cl), 90(s,cl), 103(s,cl), 171(s), 410(s,cl), 431(s,cl), 451(s,cl), 456(s,cl), 474(s,cl), 490(s,cl), 500(s,cl), 520(s,cl), 536(m, cl), 558(m, cl), 583(w, cl), 598(w, cl), 617(w,cl), 630(m), 731(m), 1084(s), 1201(br,w), 1413(vs), 1470 (s), 1616(vs), 1815(w), 2030(w), 2107(w), 2358(w), 2682(m), 3044(m), 3093(m), 3177(s), 3276(s), 3381(vs)

the lines of the separate materials appear in the complex spectrum giving a way to rapidly identify complexed $PbCl_2$. It is worth noticing that at 10 K strong narrowing of Raman lines occurs which separates very well close modes in the spectra.

Of course the computation the vibrational lines for the three compounds is somewhat boresome but this listing seems to us absolutely necessary to pinpoint the signature of the complex. The Raman (at 10 K) and IR phonons of $PbCl_2$ and thiourea are listed in Table 1. For comparison purposes, it is very intersting to quote here the modes of thiourea found at room temperature using FT-Raman (in cm^{-1}): 63 (s), 101, 117 (vs), 401 (w), 479 (m), 571 (w), 733 (s), 1093 (m), 1372, 1383 (w), 1471, 1485 (vw), 1613, 1635 (vw), 3183 (s, m), 3234, 3282, 3373 (m,w). Table 2 computes the lattice and intramolecular modes of the complex.

TABLE 2: Vibrational frequencies of complex $PbCl_2.2[(SC(NH_2)_2]$ (in cm^{-1}).
w: weak, m: medium, s: strong, cl: cluster (the band are not well resolved).

$PbCl_2.2[(SC(NH_2)_2]$	
Raman 10 K	IR (Room temperature)
Lattice modes	
43(w), 47(m), 60(s), 74(s), 82(w), 90(s), 101(m), 108(vw), 120(w), 123(w), 137(m), 149(s), 156(w), 161(m), 170(m), 197(vw), 207(vs)	70(m), 85(m), 94(s), 122(s), 139(s), 152(s), 180(s), 207(m)
Intramolecular modes	
400(w), 406(m), 416(w), 470(vw), 475(vs), 478(m), 526(w), 551(vw), 603(vw), 613(m), 708(s), 714(vs), 717(m), 742(vw), 759(w), 1089(vs), 1098(vs), 1103(vw), 1400(vw), 1424, 1436(m), 1504(m), 1513(m), 1615(m), 3209(m), 3300(s), 3369(s)	373(vw), 399(vw), 442(m), 474, 489, 502(vw), 510(vw), 520(vw), 530(vw), 540(vs), 599(m), 705(s), 1040(w), 1103(m), 1208(w), 1388(s), 1416(s), 1476(vw), 1504(w), 1618(vs), 2669(w), 3026(cl, m), 3133(cl, s), 3174(vs), 3276(s), 3336(cl ,s), 3361(vs)

For clarity we present in Fig. 2 the far infrared spectra of the three materials of this study, in Fig. 3 the infrared spectra for intramolecular modes, Figs. 4 and 5 display the Raman spectra. The region of 3000 cm^{-1} wavenumbers is not shown here for conciseness but the lines are listed in the tables.

Coincidental lines

(i)We note the presence of lattice modes (and of also intramolecular modes) at the same frequencies in Raman and IR spectra of the complex violating the mutual exclusion rule for centrosymmetric crystals. This is in agreement with the spatial group $Pna2_1$. Moreover, from Tables 1 and 2, it can be seen that numerous lines lead chloride and thiourea occur in the spectra of the complex, with frequency shifts due to crystal field effects, since the molecules in the complex see a different environment than in the free state.

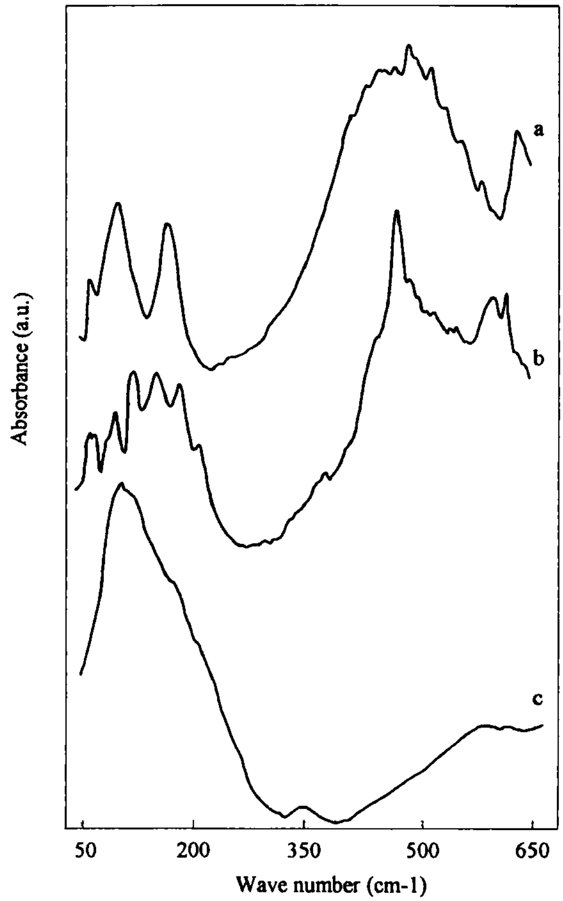

FIG. 2. Far Fourier-transform infrared spectra at room temperature (in absorbance) of thiourea (a), complex (b) and $PbCl_2$(c).

Group frequency analysis

(i) After Vijay,[2] the NH_2 modes in thiourea are strongly mixed with the out-of-plane, and stretch CS modes (481, torsional, wag, 735 cm^{-1}, rock). The 1372-1383 cm^{-1} modes are a mixing of CN, CS-stretchings, NCN deformation, and NH_2 rocking. In IR all these vibrations appear at 490, 731, and 1413 cm^{-1}. (ii) The symmetric stretching CN lines of solid state thiourea are located at 1413 (IR) and

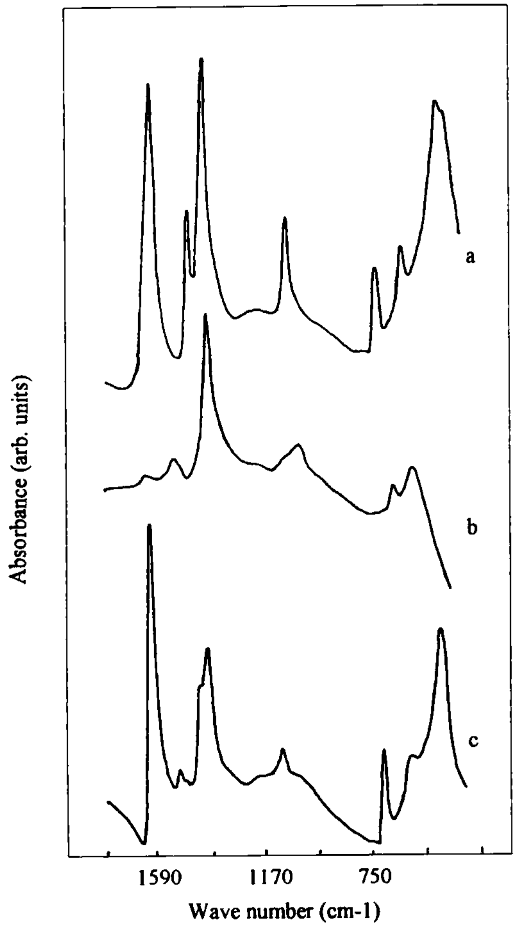

FIG. 3. Fourier-transform infrared spectra (intramolecular modes) at room temperature (in absorbance) of thiourea (a), $PbCl_2$(b), and complex (c).

1386 cm^{-1} (Raman, 10 K), the antisymmetric mode should appear at higher frequency, it was detected in our experiments at 1471 or 1485 cm^{-1} (FT-Raman).(iii) In the complex the stretching CS modes and NH_2 modes are found at 471 and 705 cm^{-1} in IR, and at 471, 475, 478, and 708-717 cm^{-1} in Raman (10 K). The -NH_2 group in the complex yields respectively the symmetric and antisymmetric stretching at 3300, and 3369 cm^{-1}, the rocking modes at 1089 and

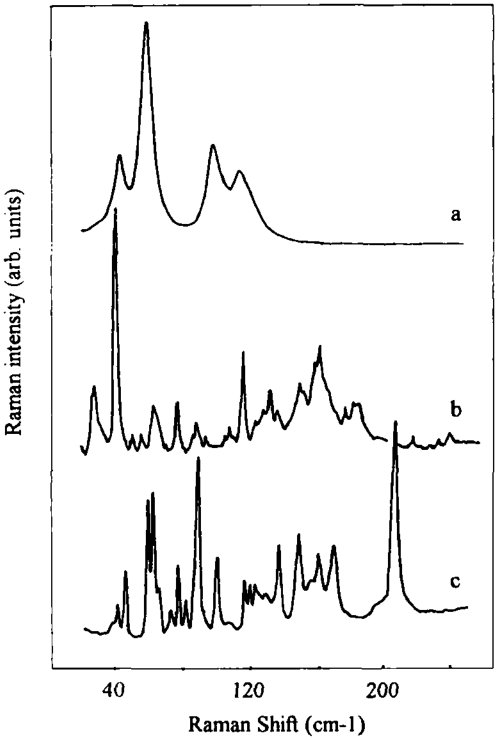

FIG. 4. Raman spectra of external modes of thiourea (a) at 293 K, $PbCl_2$(b) at 10 K, and complex (c) at 10 K.

1098 cm^{-1} (Raman) and 1103 cm^{-1} (IR), the bending mode at 1615 cm^{-1} (Raman), out-of -plane and wagging modes are at 481 cm^{-1}. In the complex, at 10 K, we ascribe the lines at 1400, 1424, 1436, 1504 and 1513 cm^{-1} to CN vibrations.[3,4] (v) Concerning the CS stretching mode we recall that previous studies on thiourea based on molecular calculations show that it is located mainly near 737 cm^{-1} (70% in potential energy distribution) with a small contribution near 1406 cm^{-1} (17%).[2]

Line shifts between the Raman spectra of thiourea and the complex

(i) The shifts of frequency between pristine thiourea and thiourea ligand in the lead chloride complex can be discussed in relationship to their structures,

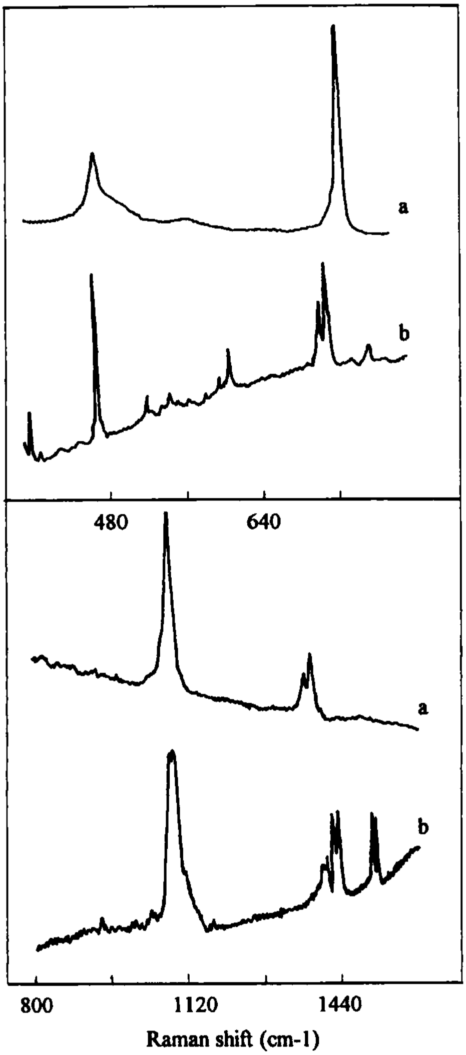

FIG. 5. Raman spectra of internal modes of thiourea (a) at 293 K and complex (b) at 10 K.

particularly with respect to subtle bonding differences in both compounds. The C-S and C-N bond lengths amount 1.71 Å and 1.33 Å respectively at ambient temperature in crystalline thiourea. In the lead chloride complex, thiourea molecules have two distinct C-S bonds (1.68 Å and 1.78 Å) and four distinct C-N bondings resulting from the unusual coordination of lead (1.40, 1.35, 1.32, 1.34 Å) and from intermolecular links. (ii) At room temperature the FT Raman spectra show the CS stretch at 737 cm^{-1} in thiourea and at 712 cm^{-1} in the complex with a very weak shoulder at 740 cm^{-1}. These shifts can be expected for there is stretching of one of the CS bonds and shortening of the other one. (iii) The bond length variations are qualitatively well reproduced in the spectra of the complex. Since one of the CN bonds is quite short it induces a frequency shift towards 1513 cm^{-1}. For the CS frequencies at 10 K a triplet appears at 708, 714, and 717 cm^{-1} (longer CS bond) accompanied with weak lines at 742 and 759 cm^{-1} (shorter CS bond).

In summary, we have presented in this letter new vibrational results on lead chloride and thiourea lead chloride complex. Low temperature experiments reveal lines with very good spectral separation. A qualitative assignment has been made by considering CN and CS bond lengths variations from thiourea to the complex. The spectral data agree well with the seven-coordination environment of lead in the complex. We notice that crystal field effects not considered here may also play a dominant role in the interpretation of vibrational spectra of the complex.

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