NQR Investigation of Intercalates and Complexes of Cadmium and Lead Iodides with Pyridine, Aniline, and Piperidine

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^{127}I and ^{14}N NQR have been investigated in two cadmium idodide – pyridine compounds, the intercalate CdI_2+5.9 pyridine and the CdI_2Py_2 complex. In the intercalate, iodine is mainly ionic and nitrogen like in pure pyridine; in the complex, iodine exhibits 30% covalency while nitrogen, coordinated to the central cadmium atom of the complex, and presents coupling constants e^2Qq and η smaller than in pure pyridine. The difference between the two compounds is also revealed by the thermal coefficient of the quadrupole coupling constants and the relaxation. Results on the other title compounds are also given.

Key words: Cadmium Iodide; Layered Structure; Intercalation; Pyridine; Nitrogen-14 NQR.

Introduction

Compounds of cadmium iodide and pyridine are members of a series where some members are intercalates like $CdI_2+5.9$ pyridine while others are complexes like CdI_2Py_2. It was of interest to study the two compounds of CdI_2 and the differences between them. CdI_2 has a layered structure in which sandwiches made of a cadmium atom layer between two iodine atom layers are stacked, held together by Van der Waals forces. Between these sandwiches, pyridine molecules find room to make the $CdI_2+5.9$ pyridine intercalate. In the complex, pyridine molecules are bound to the cadmium atom by electronic transfer from the pyridine nitrogen atom Ione pair. In the series, cadmium may be replaced by lead, copper, zinc, beryllium etc., and the halogen may be chlorine or bromine. Organic molecules other than pyridine, such ase aniline [1], can also be intercalated.

NQR relies on the interaction between the electric quadrupole moment of some atomic nuclei and the electric field gradient (efg) at the location of the resonant nuclei, and it is very sensitive to electronic charge modifications in the sample under study, modifications which may be due to changes in the chemical bonds and/or environmental conditions such as weak Van der Waals interactions or stronger intermolecular bonds leading to intermolecular complexes.

For a long time, intercalates, clathrates and inclusion compounds have attracted wide interest among NQR spectroscopists. Some of the previous studies have been on nitrogen N_2 in β-quinol clathrate [2], urea or thiourea inclusion compounds [3, 4], graphite intercalates with NH_3 [5] and $SnCl_6$ [6], intercalates of transition metal chalcogenides [7, 8] and intercalates of PbI_2 with aromatic compounds [9]. In the $N_2-\beta$-quinol clathrate, the nitrogen guest molecules are retained in three dimensional host cages, while in the urea or thiourea inclusion compounds, one-dimensional channels accommodate nonbranched long chain aliphatics or small molecules like carbon tetrachloride, dioxane or trioxane. Layered compounds like graphite, metal chalcogenides, and metal dihalogenides constitute another, bidimensional, possibility. The present investigation of the nitrogen-14 NQR in the $CdI_2+5.9$ Py intercalate and CdI_2Py_2 complex can be considered as an extension of some previous studies made some years ago on charge transfer complexes and inclusion compounds [3, 10, 11].

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$CdI_2+5.9$ Pyridine Intercalate

The intercalate is prepared by slow precipitation from an excess of pyridine under the action of ultrasonic radiation. The measured composition of the intercalate is 1 : 5.9, the hexagonal layered structure of pure CdI_2 being preserved.

Iodine Resonance

In the intercalate, the iodine resonance consists of only one strong resonance at 57.45 MHz (77 K). In fact it is a doublet made of two close lines as revealed by a slow beat visible on the echo signal. As no other lines were found that would correspond, associated to the 57.45 MHz doublet, to a value of η being between 0 and 1, the doublet is considered as corresponding to the two transitions, $1/2-3/2$ and $3/2-5/2$; the asymmetry parameter of the electric field gradient is thus very close to 1. Such as value of η, though high and unexplained so far, is not exceptional, as in the similar intercalate PbI_2+pyridine, $\eta=0.91$, or 0.78 according to the method employed for preparing the sample (see below in this paper). The low frequency of the resonance, 57.45 MHz at 77 K, is due to the ionic character of the bond between iodine and cadmium: the ionicity is estimated to 90%. In addition, the temperature coefficient of the resonance frequency (Fig. 1) is positive ($+5$ kHz · K^{-1}), which is understandable if the effect of the longitudinal motions on the lattice contribution to the efg seen by iodine nuclei is larger than the averaging effect of torsional motions, usually resulting in a diminution of the resonance frequency upon increase of the temperature.

Nitrogen Resonance

The nitrogen ν_+ and ν_- resonance lines in the intercalate were found to be close to those in pure pyridine:

	CdI_2+5.9 pyridine Intercalate (80 K)	Pure pyridine (77 K) (average over 4 sites)
ν_+	3 835.5 kHz	3 891 kHz
ν_-	2 993.3 kHz	2 984 kHz
e^2Qq	4 552.5 kHz	4 584 kHz
η	0.370	0.396

This result suggests the pyridine molecules are not chemically bound to the remainder of the crystal or, at least, the nitrogen electronic lone pair is not involved; the pyridine molecules are obviously retained in their positions by Van der Waals forces.

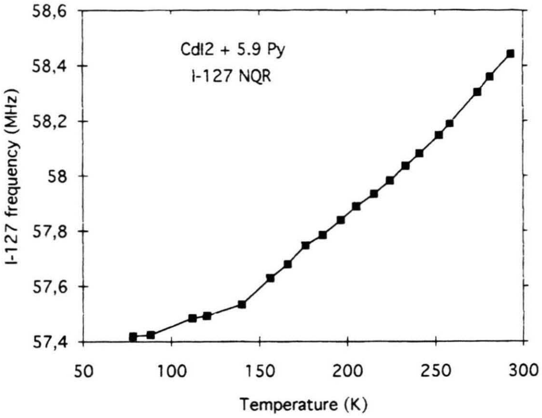

Fig. 1. Iodine ^{127}I resonance frequencies (MHz) in the CdI_2+5.9 pyridine intercalate, as a function of temperature.

The thermal coefficient for the resonance frequency ν_+ at 80 K (Fig. 2) is -1.4 kHz · K^{-1}, a value much higher than -0.35 kHz · K^{-1} found for the globular molecule compound hexamethylenetetramine (HMTA) [12]. Two reasons can explain the high value of the temperature coefficient: i) a small energy, $h\nu_t$, of the torsional motion in the Bayer model, ii) a smaller value of the inertial moment of the pyridine molecule compared to HMTA.

It may be pointed out that in the intercalate the resonance of the pyridine molecules can be observed at temperatures well above (296 K) the melting point of pure pyridine (231 K) which looks paradoxical as the strong change of the resonance frequency with temperature suggests that the pyridine molecules are more loosely retained in the intercalate than in pure pyridine.

CdI_2Py_2 Complex

The complex is obtained by mixing a water (or alcohol) solution of cadmium iodide with liquid pyridine solution with volume ratio 1:2. The CdI_2Py_2 unit is tetrahedral with the cadmium atom at the tetrahedron centre [13].

Iodine Resonance

Preliminary iodine NQR, and bromine, investigations of MX_2Py_2 complexes (M = Cd, Zn, Hg and X = Br, I) were reported earlier [11]. In CdI_2Py_2 the iodine resonance is characterized by the presence of two inequiva-

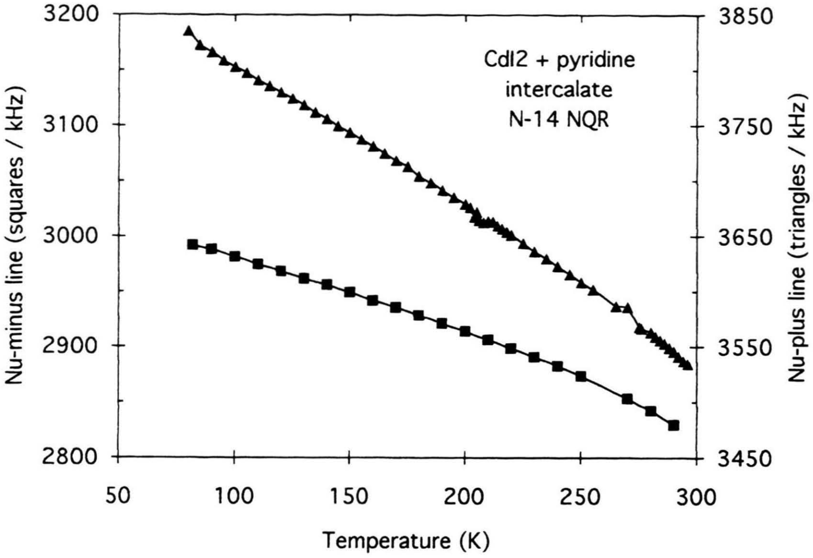

Fig. 2. ν_+ (triangles) and ν_- (squares) nitrogen ^{14}N resonance frequencies (kHz) in the CdI_2+5.9 pyridine intercalate, as a function of temperature and with the same 400 kHz scale, for both resonances.

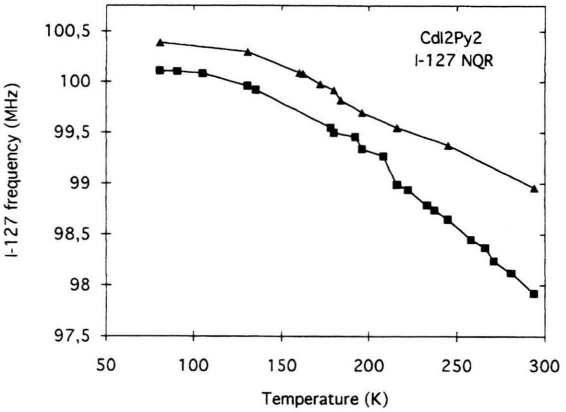

Fig. 3. The ^{127}I 1/2 – 3/2 resonance frequencies (MHz) in the CdI_2Py_2 complex, as a function of temperature (two sites).

lent sites, and the asymmetry parameter close to zero is the indication of a pure "σ" I-Cd bond.

Transition	Frequencies (MHz)	Average freq. (MHz)	Av.e^2Qq (MHz)	Av. Eta
1/2 – 3/2	100.08 – 100.41	100.25	666.32	0.051
3/2 – 5/2	199.60 – 200.04	199.82		

The 1/2 – 3/2 resonances, near 100 MHz, are in the same region as those of the other similar complexes [11] and indicate a 30% covalency character. The temperature coefficient is negative, as usual for molecular compounds (Figure 3).

Nitrogen Resonance

We wished to compare the NQR data in the intercalate to those in the complex. The latter do not seem to have been reported so far. Results on similar compounds, obtained by Hsieh et al. [14] with double NMR and NQR technique, were used as a guide for searching the resonances in CdI_2Py_2. The frequencies are quite similar to those in the series of the zinc chloride, bromide and iodide complexed with two pyridine molecules. Then, the guess was that the CdI_2Py_2 resonances should be close to those of $CdCl_2Py_2$, studied by Hsieh et al. [14]. The result was quite different:

	CdI_2Py_2 (85 K) (this work)	$CdCl_2Py_2$ (77 K) [14]	Pure pyridine (77 K) (average over 4 sites)
ν_+	2510.3 kHz	2850 kHz	3891 kHz
ν_-	2120.5 kHz	2298 kHz	2984 kHz
e^2Qq	3087.2 kHz	3432 kHz	4584 kHz
η	0.253	0.320	0.396

It took a long time to find the resonances in CdI_2Py_2 because, the frequencies being different from those in $CdCl_2Py_2$, the search had to be made over a large frequency range; in addition, the relaxation time being of the order of ten seconds, integration of a single signal needed more than one hour and runs were made with 5 kHz steps.

The data for pure pyridine are also shown for comparison: the decreases in e^2Qq and η indicate the change in

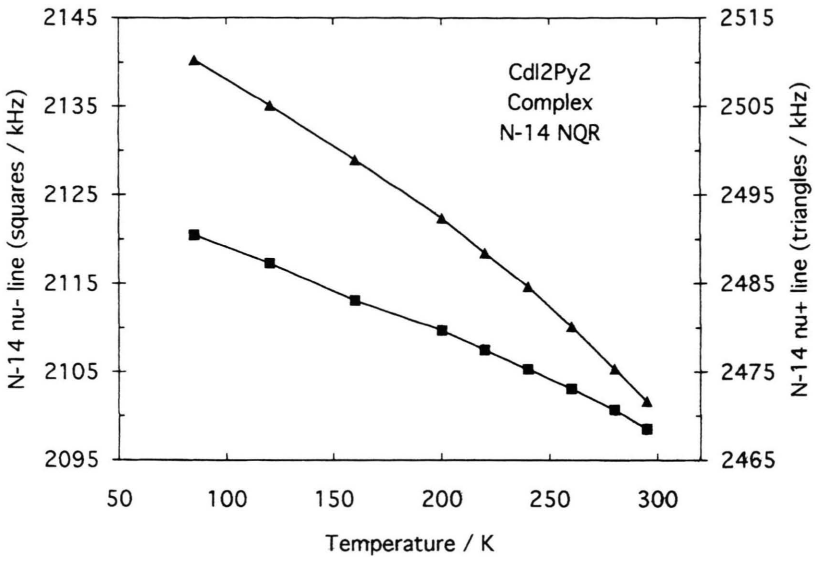

Fig. 4. ν_+ (triangles) and ν_- (squares) nitrogen ^{14}N resonance frequencies (kHz) in the CdI_2Py_2 complex, as a function of temperature and with the same 400 kHz frequency scale, except for the origin, as for the intercalate (left) and with an appropriate scale of 50 kHz (right).

the lone pair population on the pyridinic nitrogen atom due to complexation. The decrease observed when chlorine is replaced by iodine in the cadmium complexes, whereas no significant changes are observed in the corresponding zinc complexes [14], suggests that the structure of the CdI_2Py_2 molecule is different from that of $CdCl_2Py_2$, resulting in an hybridization change. From the literature it appears that the cadmium dichloride dipyridine molecule is planar [15] while the cadmium diiodide dipyridine complex is tetrahedral [12], as well as the zinc complexes [16].

As iodine shows two resonances indicating two nonequivalent sites, a second set of nitrogen resonances was expected. It is also expected from the presence of two sets of nitrogen resonances in the zinc complexes [14]: but none was found. It may have escaped the search if its relaxation time is longer than that of the recorded set.

The temperature dependence, as it appears from a few measurements (Fig. 4), shows a small temperature coefficient, about 0.28 $kHz \cdot K^{-1}$ and 0.17 $kHz \cdot K^{-1}$ for ν_+ and ν_- respectively. The pyridine molecules, being part of the large CdI_2Py_2 molecule, experience torsional oscillations of small amplitude. The oscillations are partly of intramolecular origin and partly due to motion of the bulk molecule itself. The strong bonding of the pyridine molecules to the cadmium atom and the large inertial moment of the bulk CdI_2Py_2 molecule explain the small amplitude of the motion of the pyridine molecules.

No systematic study of the relaxation time was made; however, determinations at a very few temperatures showed a relaxation time, corresponding to the recovery of two thirds of the signal, of about ten seconds.

Other Compounds Investigated

Other compounds of the series have been prepared by various methods and their iodine resonance was observed. The nitrogen resonances were not searched for lack of time of because the searches, when carried out, remained unsuccessful, quite probably because of the small size of the samples and/or a too narrow range of frequencies explored.

a) CdI_2+Piperidine and Aniline Compounds

Cadmium iodide forms complexes with piperidine and aniline. The composition of these complexes equals 1 : 2. The ^{127}I NQR frequencies at 77 K are the same as the ones given in [1, 9].

b) PbI_2+Pyridine Compounds

Three samples were prepared, one under vacuum (I), one by slow evaporation (II) and one under ultrasound irradiation (III). Sample (III) gives only one resonance (two lines corresponding to transitions 1/2 – 3/2 and 3/2 – 5/2) while samples (I) and (II) give two resonances, indicating the presence of two crystalline forms

(Fig. 5) lines in sample (I) are narrow and well separated whereas in sample (II) they overlap. Frequencies and qcc at 77 K are as follows:

	$\nu_{1/2-3/2}$	$\nu_{3/2-5/2}$	e^2Qq	η
Vacuum:	75.30 MHz	80.95 MHz	301.90 MHz	0.91
(or slow evaporation):	76.30 MHz	92.10 MHz	335.56 MHz	0.78
Ultrasound:	75.52 MHz	81.17 MHz	302.75 MHz	0.91

The frequency temperature coefficients of the resonances related to $\eta = 0.91$ (set a) are positive (see [1]). That is consistent with the result for the CdI_2+5.9 pyridine intercalate. But in the literature a chain structure is described for a compound synthesized by vacuum evaporation [17], suggesting that the compound has a one-dimensional arrangement. The second set of lines (b) relates probably to a complex with composition 1 : 1.

c) PbI_2+Aniline Compounds

These compounds were also prepared by vacuum (I) or slow (II) evaporation of the excess aniline and also under ultrasonic irradiation (III). Samples obtained by method (I) have NQR spectra with two very different sets, *a* and *b*, of resonance lines for each transition, indicating the presence of two distinct crystalline forms. One set (a) is probably related to the intercalate structure with a 6-layered packing of molecules [18] and composition 1 : 3 (the accurate determination of the composition is difficult due to the adsorption of the aniline molecules at the crystal surface). The second set is expected to correspond to the complex.

– 1 : 3 Intercalate (set of lines a)

Aniline forms a 1 : 3 intercalate with PbI_2. It is characterized by low enough NQR frequencies at 77 K (35.08 MHz for transition $\Delta m = 1/2 - 3/2$ and 39.85 MHz for transition $\Delta m = 3/2 - 5/2$), an 85% asymmetry parameter and a positive temperature coefficient of the ^{127}I resonance frequency. The ionicity of the Pb-I bond is very large (~ 93%).

– 1 : 1 Complex (set of lines b)

This complex was obtained as the second form, b, in the mixture of the intercalate form, and is the only form obtained with method (III). Samples obtained with both methods yield the same 54% asymmetry parameter and very close q.c.c. values (377.50 and 370.25 MHz, respectively). These values of the NQR parameters suggest an important intermolecular coordination of the iodine atoms. The temperature coefficient of the resonance frequency is negative, as expected for a molecular compound.

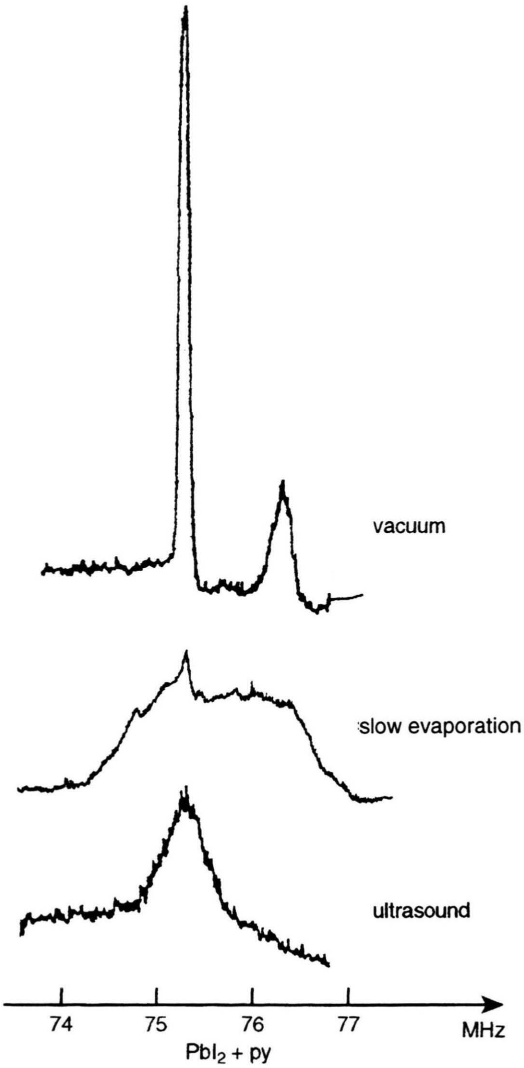

Fig. 5. ^{127}I NQR lines at 77 K in the three samples of PbI_2+pyridine intercalate. From top to bottom: samples prepared by evaporation under vacuum, by slow evaporation, and under ultrasounds.

d) PbI_2+Piperidine Compounds

– PbI_2+8 piperidine

This compound was synthesized under ultrasonic radiation. Its ^{127}I NQR frequencies at 77 K are very low:

$\nu_{1/2-3/2}$	$\nu_{3/2-5/2}$	e^2Qq	η
17.10 MHz	20.21 MHz	72.87 MHz	0.87

The temperature dependence of the NQR lines in this compound was not studied. The high ionicity of the bond Pb-I (~97%) is an indication for rather free piperidine molecules; that is confirmed by IR-spectroscopy [19] data.

- PbI_2+1.5 piperidine

This form was synthesized by slow evaporation from an excess of piperidine. The NQR frequency for the transition $\Delta m = 1/2 - 3/2$ is 82.35 MHz. This rather high value shows a significant interaction of the metal ion with the nitrogen atom.

Conclusion

This study of two cadmium iodide+pyridine compounds brings new results in the field of the inclusion/intercalated compounds and complexes. It has been possible to study both the iodine and nitrogen resonances and compare the intercalate and complex with the pure components. That seems to be the first report of a nitrogen resonance in a layered intercalated compound. The resonances were not only searched and found but their temperature dependence was also recorded. The results obtained show several interesting features: in the intercalate, the asymmetry of the electric field gradient at the iodine site is quite high while it is nearly zero in the complex; the thermal coefficient of the iodine resonance frequencies is positive. The crystal structure is stable enough to permit the observation of the pyridine nitrogen resonance at temperatures well above the melting point of pure pyridine, though torsional motions have a large amplitude resulting in a high thermal coefficient for the resonance frequencies. Oppositely, in the complex, the thermal coefficient in unusually small; in addition, there is a noticeable covalent character of the iodine-cadmium bond and a large charge transfer from the nitrogen lone pair towards the cadmium atom.

Finally, as the cadmium iodide + pyridine couple is member of a large family of similar halides + organic nitrogen heterocyclic compounds, the reported study suggests further investigation of this family of lamellar compounds, especially through the study of nitrogen resonances in compounds in which iodine resonances have already been detected.

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