Polymorphous phase transition in the clathrate $[Cd(py)_4(NO_3)_2]\cdot 2py$ at 221 K

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The phase transition observed in the system pyridine–cadmium nitrate at 221 K is accounted for by a polymorphous transformation of the clathrate $[Cd(py)_4(NO_3)_2]\cdot 2py$ and is caused by a change in the coordination metal–nitrate bond in the host–complex molecule.

X-ray studies of compounds of the empirical formula '$MX_2\cdot 6py$' [M is metal(II); X is a univalent anion and py is pyridine] have disproved the opinion that they are similar to hexammine–metal complexes.[1–4] The central atom is octahedrally coordinated by only four pyridine ligands in the compounds while the fifth and the sixth coordination sites are in the *trans*–position and are occupied by the anionic ligands X. The remaining two pyridine molecules are not connected chemically and are held in the structure by van der Waals forces. This is why the above compounds are classified with clathrates, having a complex host-component and pyridine as a guest, $[M(py)_4X_2]\cdot 2py$.

Of particular interest is a group of clathrates with nitrate as X, *i.e.* $[M(py)_4(NO_3)_2]\cdot 2py$,[2,3] since only one compound, $[Cu(py)_4(NO_3)_2]$[5] of the host complexes $[M(py)_4(NO_3)_2]$ (M = Cd, Co, Ni, Zn), has been obtained. Contact stabilization phenomenon observed in similar systems[6,7] suggests that the complexes involved can be unstable as separate phases, while their molecules form and exist in clathrates due to favourable packing with the guest molecules. In the case of the Zn-compound this has been corroborated by detailed study of the pyridine–zinc nitrate system.[8] Therefore, clathrates of this type offer the possibility of studying complexes that cannot be isolated as separate compounds. This communication discusses a Raman spectral study of the phase transition in the pyridine–cadmium nitrate system caused by a change in the nature of the metal–nitrate coordination bond in the complex host molecule in the clathrate phase $[Cd(py)_4(NO_3)_2]\cdot 2py$.

Pyridine (p.a.) purified by distilling over BaO and kept over zeolite 3A ('reinst') contained 0.017(2) mass%[†] of water and melted at −43.6 to 42.8 °C (*cf.* lit.[9] −42.7 °C). The clathrate $[Cd(py)_4(NO_3)_2]\cdot 2py$ was obtained by a two-stage recrystallization of $Cd(NO_3)_2\cdot 4H_2O$ (p.a.) in pyridine.[3] Analysis: calc. for $[Cd(py)_4(NO_3)_2]\cdot 2py$ (%): Cd, 15.8; py, 66.8. Found: Cd, 15.7(1); py, 66.5(5); H_2O, 0. The powdered clathrate was obtained by saturating the complex $[Cd(py)_3(NO_3)_2]$ with pyridine vapour in a desiccator.[10] The complex $[Cd(py)_3(NO_3)_2]$ was obtained by decomposing the crystalline clathrate in air for one or two days, until the product no longer smelt of pyridine. Analysis: calc. for $[Cd(py)_3(NO_3)_2]$ (%): Cd, 18.81; py, 45.5. Found: Cd, 18.79(8); py, 45.8(3); H_2O, 0. The complex $[Cu(py)_4(NO_3)_2]$ was obtained using the procedure described in ref. 5 by decomposing the clathrate crystals of $[Cu(py)_4(NO_3)_2]\cdot 2py$, synthesized as in ref. 3. Analysis: calc. for $[Cu(py)_4(NO_3)_2]$ (%): Cu, 12.61; py, 62.8. Found: Cu, 12.58(5); py, 61.9(4). KNO_3 (p.) was also used. Analysis of the compounds was carried out by procedures described elsewhere.[8]

The phase diagram of the system was studied by DTA and solubility techniques; experimental details are discussed in ref. 8.

The Raman spectra were registered on a Raman-spectrometer Triplemate (Spex, USA). The spectra were obtained with the 488 nm line of an Ar^+-laser and recordered with a multiscan detector, O-SMA. A powdery clathrate sample was sealed in a thin-wall glass ampoule and placed in the cold-carrier of an optical cryostat with a regulated temperature (LT-110 K, APD-Cryogenics, England). The accuracy of the temperature regime of the cold-carrier was ±0.1 K; the temperature of the sample rose to some extent (2–3 K) during the experiment.

The phase diagram of the pyridine–cadmium nitrate system in the studied range is shown in Figure 1. Two compounds are observed in the system: the clathrate $[Cd(py)_4(NO_3)_2]\cdot 2py$, melting incongruently at 379.2(5) K, and the complex $[Cd(py)_3(NO_3)_2]$, melting congruently at 438.7(4) K. No compound of the host complex $[Cd(py)_4(NO_3)_2]$ forms in the system.

At 221.4(4) K a phase transition occurs in the system. The corresponding heat effect is approximately one order of magnitude weaker than the melting effects of the compounds and the eutectic mixture and its maximum corresponds to the clathrate composition. Figure 2 shows the Raman spectra of the clathrate sample at various temperatures above and below the transition point. The spectra of the clathrate, the complex $[Cu(py)_4(NO_3)_2]$, pyridine and potassium nitrate at room temperature, making it possible to discern in the clathrate spectra the vibrations of its main components, the lattice, pyridine (ligand and guest) and anion NO_3^-, are illustrated in Figure 3.

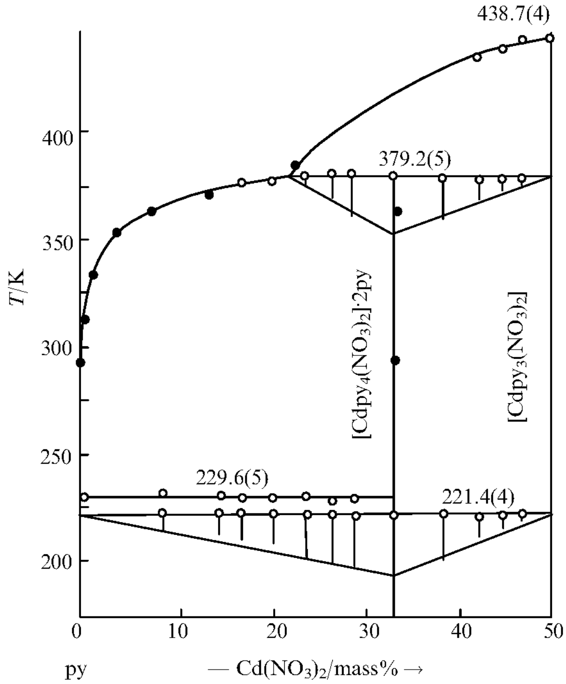

Figure 1 Phase diagram of the pyridine–cadmium nitrate system in the studied range. Open circles, method DTA; solid circles, solubility method. The values of the heat effects of the polymorphous transition are increased tenfold relative to the values of the effects of the incongruent melting clathrate.

[†] Standard deviations of the last meaningful figure are given in brackets throughout.

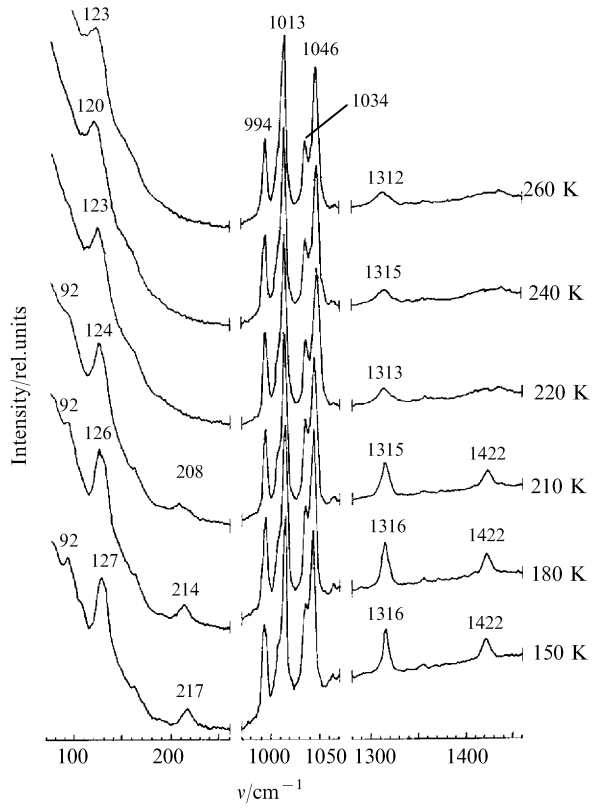

Figure 2 Raman spectra of the [Cdpy$_4$(NO$_3$)$_2$]·2py clathrate at different temperatures (selected fragments).

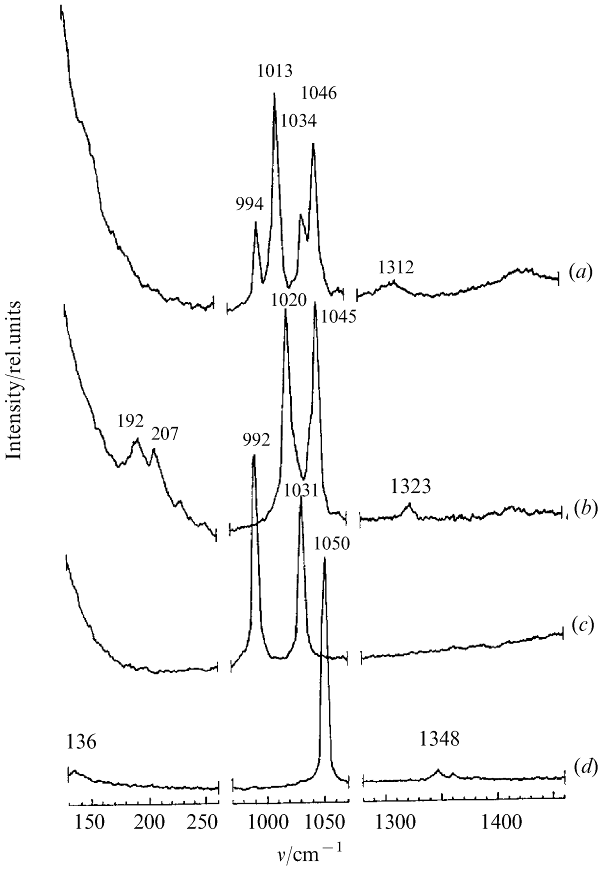

Figure 3 Raman spectra of the clathrate [Cd py$_4$(NO$_3$)$_2$]·2py (*a*), complex [Cu py$_4$(NO$_3$)$_2$] (*b*), pyridine (*c*) and potassium nitrate (*d*) at room temperature (selected fragments).

As is seen from Figure 2, no appreciable jump-wise changes were observed over all the studied range (80–200 cm^{-1}) of the lattice vibrations of the clathrate. The same is true of the breathing vibrations of the pyridine rings in the range 990–1050 cm^{-1}. Only the band at 1046 cm^{-1}, which is due to accidental degeneration of pyridine (host) and the anion NO_3^- vibrations (*cf.* Figure 3), shows a tendency toward smaller values at low temperatures (*ca.* 4 cm^{-1}); this is caused by a shift in the frequency or a change in the intensity of the totally symmetric stretching mode of NO_3^-. Thus, consideration of these fragments of the spectrum rules out decomposition of the clathrate into solid pyridine and the complex [Cd(py)$_3$(NO$_3$)$_2$] below the transition point (decomposition of an 'endothermic' compound[11]) and suggests that the phase transition observed in the system is due to a polymorphous transformation of the clathrate, which results in the phase diagram illustrated in Figure 1.

Figure 2 also shows that the main spectral effect of the polymorphous transformation of the clathrate is the disappearance of the band near 214 cm^{-1} and a sharp decrease in the intensity of the bands 1315 and 1422 cm^{-1} at about 220 K. The low-frequency mode should be attributed to the vibrations of the M–O_{NO_2} bond, and the high-frequency one to the stretching valent vibrations of NO_3^- resulting from the degenerated E' mode of the free anion. All this suggests the following scheme for the observed phase transition. A change in the intensities of the bands involved can be accounted for by a change in the polarizability of the bonds of the (NO_3^-)–Cd–(NO_3^-) fragment rather than by the formation of new ones since the lines at 1315 and 1422 cm^{-1} are also observed at room temperature as very weak ones. As shown in ref. 3, the clathrate [Cd(py)$_4$(NO$_3$)$_2$]·2py is isostructural with [Ni(py)$_4$(NO$_3$)$_2$]·2py, the structure of which was studied to the extent of determining the atomic coordinates.[2] Its nitrate groups are terminally coordinated to the nickel atom and their planes are situated at a small angle to each other. The distance Ni–O, equal to 2.093 A, shows that the Ni–O_{NO_2} bond is a very weak donor–acceptor one, resembling the metal–oxygen bond in the case where the water molecule is coordinated in the Ni(acac)$_2$·2H$_2$O complex, where the distance Ni–O_{H_2} is equal to 2.14 A.[12] In this case the distance Ni–O(acac) is essentially shorter (2.01 A) because the atomic orbitals of the metal are included in the combined molecular orbitals of both chelates.

Because the anions NO_3^-, like chelate ligands acac, have delocalized orbitals, the orbitals may be weakly connected through the metal atom by means of its vacant orbitals. Therefore, we assume that in [Cd(py)$_4$(NO$_3$)$_2$]·2py the temperature decrease will cause the nitrate ligands and the cadmium atom in the host molecule to approach each other and (or) to turn relative each other until they are in the plane of the formation of a common molecular orbital. In this case the intensities of all modes of the (NO_3^-)–Cd–(NO_3^-) fragment should change, which is seen to occur in the clathrate spectra.

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