Investigation by vibrational spectroscopy of the complexation of poly(acrylamide) by cadmium halides

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With the general purpose of testing various inorganic sensitive membranes for ISFET, the systems poly(acrylamide) (PAam)–xCdX$_2$ (X = Cl, Br, I) have been studied for $x \leqslant 0.5$. The IR and Raman spectra show that the metal interacts with the oxygen atom of the amide group and allow the vibrations of the complexed CdX$_2$ to be characterized. A possible structure is proposed.

In 1970, Bergveld reported a new device for chemical analysis,[1] the ISFET (ion sensitive field effect transistor). ISFETs combine the advantages of ion-selective electrodes and that of microelectronic devices. In the case of heavy-ion detection some authors proposed inorganic membranes based on chalcogenide or chalcohalogenide materials.[2–4]

Furthermore, ISFET polymeric membranes have been already proposed to detect proton, alkali or alkaline earth ions.[5–7] It was tempting to use such materials for analysis of heavy ions. It is well known that polymers possessing Lewis basic groups, such as poly(acrylamide) (PAam) are able to complex inorganic cations considered as Lewis acids.[8–14]

Here we study the interaction between PAam and cadmium halides CdX$_2$ (X = Cl, Br, I) using IR and Raman spectroscopies.

Experimental

PAam (Janssen Chimica, average $M_w = 5–6 \times 10^6$), CdCl$_2$, CdBr$_2$ and CdI$_2$ (Aldrich, 99%) were used without further purification. Mixtures were prepared by stirring adequate quantities of the polymer and salt in distilled water for 12 h. The solution was then poured into glass rings placed on a PTFE surface and water was evaporated off at 50 °C under a stream of dry air. A final dehydration was performed under vacuum. Transparent and amorphous films with composition (PAam)–xCdX$_2$ are obtained for $x \leqslant 0.5$, where x is the number of cadmium halide molecules per polymer repeat unit. For $x \geqslant 0.5$, the films become opalescent. We thus chose compositions below this limit.

For the Raman and far-IR spectra, free-standing films of *ca.* 10–100 μm could be directly used. For the mid-IR experiments, a drop of solution was spread onto a silicon window in order to obtain films of a few μm thickness after water evaporation. Further dehydration was then performed *in situ* in a vacuum chamber equipped with CsI windows.

The 4000–400 and 600–50 cm^{-1} spectral ranges were measured with Nicolet 740 and Nicolet 20F FTIR spectrometers, respectively. One hundred spectra were coadded at a resolution of 4 cm^{-1}.

The Raman spectra were recorded from anhydrous films of *ca.* 100 μm thickness in the back scattering geometry using the microscope of a Dilor Omars 89 spectrometer, the 514.5 nm exciting line of an argon laser and a CCD (charge coupled device) detector. The 700–20 cm^{-1} spectral range was investigated with a resolution of 3.7 cm^{-1}.

Results and Discussion

All the IR spectra are normalized using the area of the absorption corresponding to the stretching modes of the methylene groups as these vibrations are rather insensitive to doping or N-deuteriation of PAam. The antisymmetric $\nu_{as}(CH_2)$ stretching mode is situated at 2951 cm^{-1} and the symmetric $\nu_s(CH_2)$ mode at 2929 cm^{-1} and the two components strongly overlap. The CH group of PAam gives a separated weak $\nu(CH)$ absorption at *ca.* 2865 cm^{-1} (Fig. 1). The aim of the normalization using the $\nu(CH_2)$ absorptions is to bring all the samples to a common virtual thickness for easier comparison, it being difficult to make films of controlled and reproducible thickness by the sampling procedure described above.

In the region of the NH$_2$ stretching vibrations, the pure polymer exhibits a very broad profile extending from 3100 to 3500 cm^{-1} [Fig. 1(a)]. The NH$_2$ groups are involved in intra- and inter-chain hydrogen bonds of the N—H···O=C type. It is generally presumed that $\nu_{as}(NH_2)$ corresponds to the maximum at 3336 cm^{-1} and $\nu_s(NH_2)$ to the band at

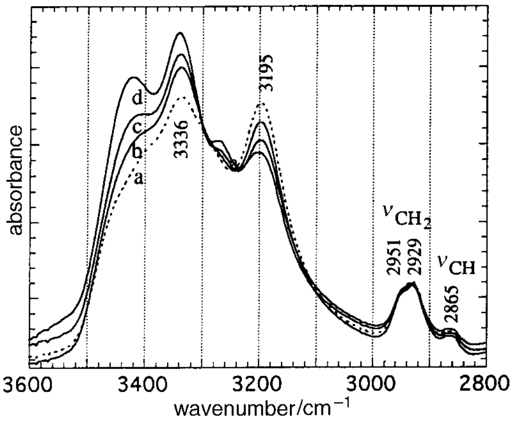

Fig. 1 IR spectra of PAam–xCdCl$_2$ mixtures: (a) $x = 0$ (pure PAam, dotted line); (b) $x = 0.1$; (c) $x = 0.2$, (c) $x = 0.33$ and (d) $x = 0.5$

3195 cm^{-1}.[9,10,15,16] However, it is also known that these vibrations can be rather strongly perturbed by Fermi-resonances with the first overtones of the amide I and II modes and with other combination modes.

Finally, a shoulder at 3420–3450 cm^{-1} can be observed for pure PAam. It does not seem to correspond to water absorptions as its intensity remains unchanged after prolonged heating under vacuum. We believe that some NH_2 groups not involved in hydrogen bonds are responsible for this high-frequency shoulder.

When the polymer is progressively doped with cadmium halides, an intensity increase is observed between 3250 and 3500 cm^{-1} whereas an intensity decrease occurs for the 3195 cm^{-1} band (Fig. 1). A similar evolution has been described by Roberts and Jenekhe[11] for the Lewis acid–base complexes formed between polyamides and $GaCl_3$. In agreement with these authors, one can infer that the Lewis acid severs $NH\cdots O{=}C$ hydrogen bond interactions and establishes stronger $Cd\cdots O{=}C$ interactions which liberate some NH_2 groups. For a better characterization of the bands which appear on doping, we have subtracted the spectrum of pure PAam from the spectra of doped PAam, with a subtraction factor such that the 3195 cm^{-1} absorption is cancelled. The results illustrated in Fig. 2 for PAam–xCdCl$_2$ show that three components are now systematically detected. Their intensity increases roughly in proportion to the salt concentration. Very similar spectral evolution was observed with the other cadmium halides (Fig. 3). The high-frequency component is assigned to $\nu_{as}(NH_2)$ of 'free' NH_2 groups. Actually, 'free' means weakly bonded, for example in $N{-}H\cdots X$ interactions with the metal halide. The frequencies of 3436, 3434 and 3430 cm^{-1} observed for X = I, Br and Cl (Fig. 3), respectively, indicate that, as expected, the $N{-}H\cdots X$ interaction is slightly weakened in the order: I < Br < Cl. The $\nu_s(NH_2)$ mode of these free NH_2 groups is more difficult to situate since there are two possible candidates at *ca.* 3340 and 3262 cm^{-1}. Empirical relationships have been established between the ν_{as} and ν_s modes of symmetric NH_2 groups.[16] For example, from the equation:

$$\nu_{as} = 0.89\nu_s + 484\ \mathrm{cm}^{-1} \qquad (1)$$

with $\nu_{as} = 3430$ cm^{-1}, ν_s is calculated at 3310 cm^{-1}, *i.e.* in between the two observed components. It is possible that $\nu_s(NH_2)$ interacts by Fermi-resonance with another mode, and in particular with the overtone of the $\delta(NH_2)$ mode (amide II) situated at 1613 cm^{-1}. It is also possible that the NH_2 groups in pure and doped PAam are highly asymmetric because one of the N−H bonds is more specifically hydrogen bonded than the other.

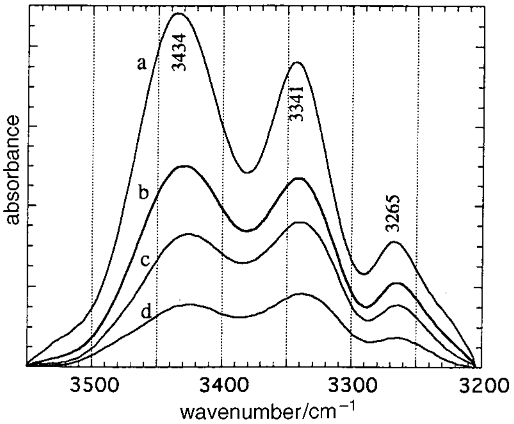

Fig. 2 Difference IR spectra PAam–xCdCl$_2$ − PAam from the data of Fig. 1 with (a) $x = 0.5$; (b) $x = 0.33$; (c) $x = 0.2$ and (d) $x = 0.1$

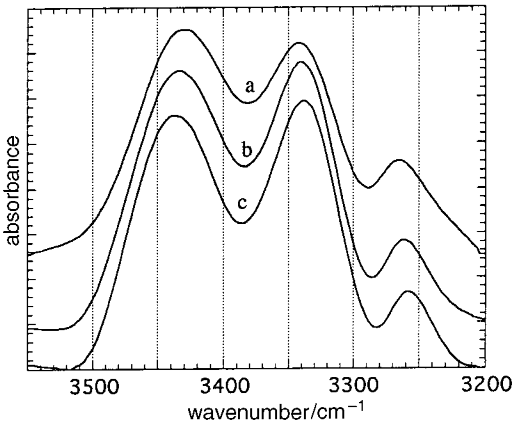

Fig. 3 Difference IR spectra PAam–xCdX$_2$ − PAam for $x = 0.33$: (a) $CdCl_2$, (b) $CdBr_2$ and (c) CdI_2

In order to clarify the situation, we have applied the isotopic dilution technique to the pure polymer and to $x = 0.33$ CdX$_2$ mixtures. By adding small amounts (5–10%) of D_2O to a H_2O solution (or small amounts of H_2O to a D_2O solution), NHD groups are created and the ν(ND) [ν(NH)] stretching vibration appears in a region which is free from any other absorptions. In addition, the quasi-diatomic N−D (or N−H) oscillator is uncoupled from other vibrational modes and can be used as a spectroscopic probe of the interactions experienced by the NHD group.

As shown in Fig. 4(d), highly N-deuteriated PAam exhibits a doublet at *ca.* 2555 and 2400 cm^{-1} assigned to the $\nu_{as}(ND_2)$ and $\nu_s(ND_2)$ modes, respectively.[9,10,15] In the spectra of weakly N-deuteriated PAam, the ν(ND) mode occurs as a single band at 2460 cm^{-1} [Fig. 1(c)]. After doping, this band shifts to 2482 cm^{-1} with $CdCl_2$ and to 2500 cm^{-1} with CdI_2. The profiles are very broad and asymmetric but, unfortunately, it is not possible to distinguish two separated components arising from the $N{-}H\cdots O{=}C$ and $N{-}H\cdots Cl$ contributions.

The same kind of observation can be made in the ν(NH) spectral range for highly deuteriated samples (Fig. 5). Finally, from the results of Fig. 4 and 5, one obtains a clear confirmation of the shift to higher frequencies of the ν(NH) or ν(ND) vibrations in the order: PAam < PAam–0.33CdCl$_2$ < PAam–0.33CdI$_2$. In addition, the isotopic ratio $\nu(NH)/\nu(ND)$ is systematically of 1.35 in all these systems. The deformation mode of the NHD group, δ(NHD), is tentatively assigned to a new absorption which appears at 1520 cm^{-1} in PAam and 1526 cm^{-1} in PAam–0.33CdCl$_2$.

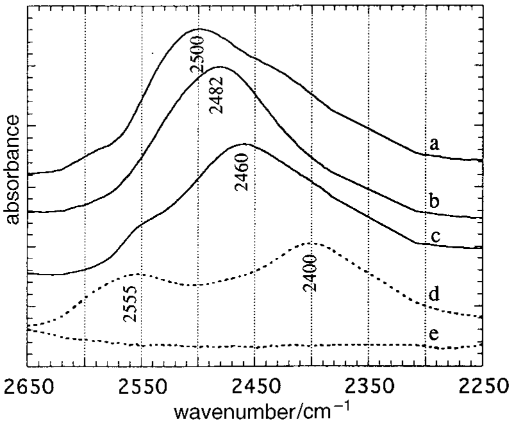

Fig. 4 ν(ND) absorption in partially N-deuteriated (a) PAam–0.33CdI$_2$; (b) PAam–0.33CdCl$_2$ and (c) PAam. The spectra of highly deuteriated PAam (d) and of hydrogenated PAam (e) are given for comparison. The intensity of spectrum (d) has been divided by 10 for convenience. A straight line has been drawn between 2380 and 2310 cm^{-1} where atmospheric CO_2 is ill compensated.

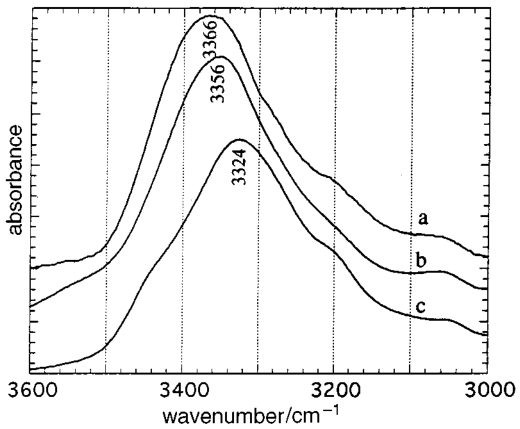

Fig. 5 ν(ND) absorption in highly deuteriated PAam–0.33CdI$_2$ (a); PAam–0.33CdCl$_2$ (b); and PAam (c)

To aid in structural elucidation of the metal–polymer interactions, it is useful also to consider the amide I and II spectral range (Fig. 6). In pure PAam, the amide I band, which has essentially a ν(C=O) character, is asymmetric and presents a maximum at 1661 cm^{-1}. One can again infer that an unresolved component due to non-hydrogen bonded C=O groups occurs above 1661 cm^{-1}. The amide II absorption, corresponding mainly to the δ(NH$_2$) vibration, is observed at 1613 cm^{-1} and the amide III of ν(CN) character at 1412 cm^{-1}. The band at 1450 cm^{-1} is assigned to the δ(CH$_2$) mode [Fig. 6(a)].

The cadmium–oxygen interaction is directly evidenced by a frequency shift of the amide I band down to 1650 cm^{-1} and of amide III band up to 1419 cm^{-1} [Fig. 6(d)]. These shifts remain small, indicating that the Lewis acid–base interaction is only slightly stronger than the hydrogen-bond interaction. As expected, the resonance within the amide group is modified by electron withdrawing from the C=O bond and this is accompanied by a small strengthening of the C—N bond. If the metal was coordinated to the nitrogen atom, reverse effects would be observed.

The amide II band is shifted from 1613 in pure PAam to 1590 cm^{-1} in PAam–0.33 CdI$_2$ and has to be associated with contributions of the 'free' NH$_2$ groups. We have seen that these 'free' oscillators present higher stretching vibrations than the N—H···O hydrogen-bonded ones; it is also expected that their deformation vibration is shifted to lower frequencies. The values of 1598 cm^{-1} (CdCl$_2$), 1594 cm^{-1} (CdBr$_2$) and 1590 cm^{-1} (CdI$_2$) at $x=0.33$, are again in agreement with the decreasing N—H···X interaction in this series.

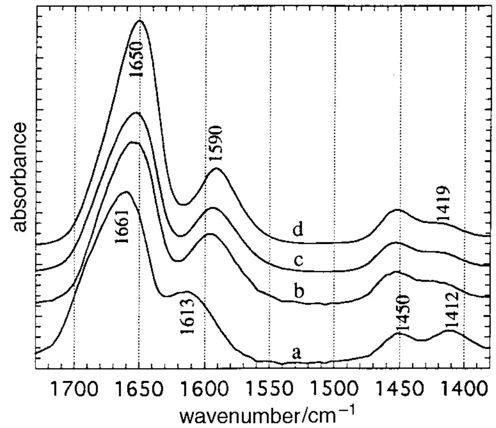

Fig. 6 Amide I, II and III IR absorptions for PAam (a); PAam–0.33CdCl$_2$ (b); PAam–0.33CdBr$_2$ (c); and PAam–0.33CdI$_2$ (d)

The low-frequency IR spectra (Fig. 7) exhibit a broad absorption between 700 and 450 cm^{-1}. This absorption involves the amide IV and V vibrations which have a δ(NCO) and γ(NH$_2$) character, respectively. Although the shape of the whole absorption pattern changes after doping, it is difficult to disentangle the various contributions. However, one can note that this absorption is red-shifted from Cl to Br and I, *i.e.* γ(NH$_2$) behaves as δ(NH$_2$).

Spectral differences between the three salts occur also below 350 cm^{-1} in a region where, in addition to vibrations of the polymer skeleton, internal vibrations of the coordinated CdX$_2$ species are situated.[17] A new absorption appears at about 230 cm^{-1} with CdCl$_2$, 148 cm^{-1} with CdBr$_2$ and 133 cm^{-1} with CdI$_2$. Similarly, the Raman spectra (Fig. 8) exhibit new features at *ca.* 229, 147 and 120 cm^{-1} in the same series.

According to literature results,[17,18] cadmium halides complexed with organic ligands have been found to adopt either a tetrahedral structure [Fig. 9(a)] or a polymeric octahedral structure [Fig. 9(b)]. Transition-metal complexes between MCl$_2$ (M = Ni, Fe, Zn, Cu, Co, ...) and malonamide have also been shown to adopt the octahedral structure of Fig. 9(c).[19]

Our results are more in favour of the tetrahedral structure. Indeed, the ν(M—X) stretching vibrations show nearly ident-

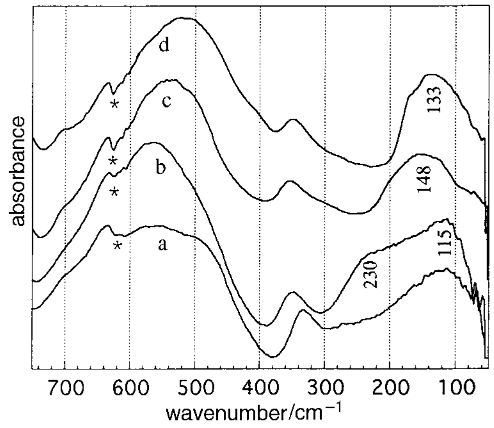

Fig. 7 Low-frequency IR spectra of PAam (a); PAam–0.33CdCl$_2$ (b); PAam–0.33CdBr$_2$ (c); and PAam–0.33CdI$_2$ (d). The asterisks indicate a region where the silicon background is not exactly compensated.

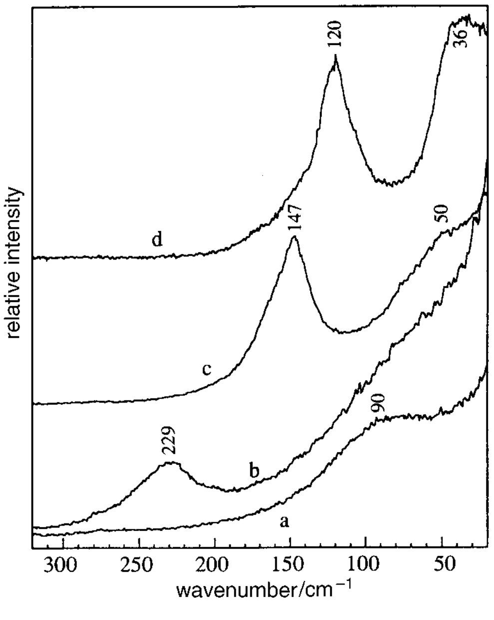

Fig. 8 Low-frequency Raman spectra of PAam (a); PAam–0.33CdCl$_2$ (b); PAam–0.33CdBr$_2$ (c); and PAam–0.33CdI$_2$ (d)

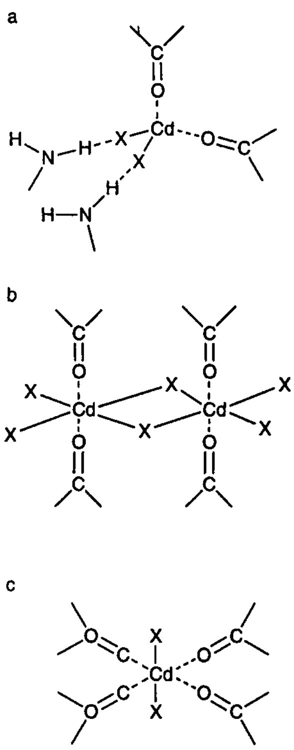

Fig. 9 Schematic representation of tetrahedral (a); polymeric octahedral (b); and monomeric octahedral complexes (c) between CdX_2 and PAam

ical IR and Raman frequencies, as expected for a bent CdX_2 molecule having similar ν_1 and ν_3 frequencies, both being IR and Raman active. On the other hand, the polymeric structure of Fig. 9(b) implies the presence of two types of Cd—X bonds and therefore of two types of stretching frequencies, the so-called bridging (ν_b) and terminal (ν_t) frequencies, which have been shown to differ according to $0.7<\nu_b/\nu_t<0.9$ in a series of MX_2 complexes.[17] If such complexes were formed between PAam and CdX_2, the spectra should reveal two distinct stretching frequencies and concentration effects should modulate their intensity ratio. Finally, the linear structure adopted by the MX_2 molecules in the monomeric octahedral structure [Fig. 9(c)] should also give rather different IR and Raman spectra since, for example, the $CdCl_2$ linear molecule in the gas phase presents a ν_1 Raman active mode at 327 cm^{-1} and a ν_3 IR active mode at 419 cm^{-1}.[17]

It must be however pointed out that our hypothesis of a tetrahedral structure has to be considered by keeping in mind that the geometry of the $CdCl_2$ complex is certainly less well defined with a polymer than with small organic ligands. Chain constraints are likely to induce a distribution of distorted tetrahedral structures. This is indicated by the broadness of the IR and Raman bands. We have concluded that the ν_1 and ν_3 average stretching frequencies are very similar. One can remark that the deformation mode ν_2 could well correspond to the Raman features appearing at about 50 cm^{-1} with $CdBr_2$ and 36 cm^{-1} with CdI_2. This mode is not clearly observed with $CdCl_2$ probably because of strong overlapping with a broad polymer band centred at *ca.* 90 cm^{-1}.

Conclusion

The IR and Raman spectra of PAam–$x$$CdX_2$ complexes (X = Cl, Br, I; $x \leqslant 0.33$) and of their partially N-deuteriated derivatives indicate that the metal is coordinated to two amide oxygen atoms in approximately tetrahedral structure. The stretching vibrations of the bent CdX_2 complexed molecules are observed at *ca.* 230, 147 and 120 cm^{-1} for X = Cl, Br and I, respectively. The deformation mode is tentatively situated at 50 (Br) and 36 (I) cm^{-1}. The halogen atoms of the bent CdX_2 species are weakly bonded to NH_2 groups. The stretching vibrations of these 'free' NH_2 groups occur at slightly higher frequency in NH···I than in NH···Br and in NH···Cl and the reverse situation is observed for the NH_2 deformation (amide II) and wagging (amide V) modes.

References

1 P. Bergveld, *IEEE Trans. Biomed. Eng.*, 1970, **17**, 70.
2 Y. G. Vlasov, E. A. Bychkov and A. V. Legin, *Sens. Actuators B*, 1992, **10**, 55.
3 M. Eldamer-Rinaudo, J. Salardenne, M. A. Subramanian and J. Portier, *Ann. Chim. Sci. Mater.*, 1995, **20**, 419.
4 M. Eldamer-Rinaudo, Thesis, University Bordeaux I, 1995.
5 A. J. Polak, S. Petty-Weeks and J. Beuhler, *Sens. Actuators*, 1986, **9**, 1.
6 P. T. McBride, J. Janata, P. A. Comte, S. D. Moss and C. Johnson, *Anal. Chim. Acta*, 1978, **101**, 239.
7 T. Gennett and W. Purdy, *Inisit*, 1991, **60**.
8 M. A. Ratner and D. F. Shriver, *MRS Bull.*, 1989, 39.
9 Y. E. Kirsh, O. P. Komarova and G. M. Lukovkin, *Eur. Polym. J.*, 1973, **9**, 1405.
10 M. K. Gupta and R. Bansil, *J. Polym. Sci.: Polym. Phys. Ed.*, 1981, **19**, 353.
11 M. F. Roberts and S. A. Jenekhe, *Macromolecules*, 1991, **24**, 3142.
12 M. Hernandez, L. Servant, J. Grondin and J. C. Lassegues, *Ionics*, 1995, **1**, 454.
13 J-C. Lassegues, J. Grondin, M. Hernandez, I. Rey, L. Servant and S-J. Wen, *New J. Chem.*, 1996, **20**, 317.
14 *Macromolecule–Metal Complexes*, ed. F. Ciardelli, E. Tsuchida and D. Wohrle, Springer-Verlag, Berlin, 1996.
15 D. Rodriguez, C. Jegat, O. Trinquet, J. Grondin and J. C. Lassegues, *Solid State Ionics*, 1993, **61**, 195.
16 N. P. G. Roeges, *A Guide to the Interpretation of Infrared Spectra of Organic Structures*, John Wiley, Chichester, 1994, pp. 179–183.
17 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 4th edn., 1986.
18 G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, 1968, **24**, 959.
19 S. H. J. De Beukeleer and H. O. Desseyn, *Spectrochim. Acta, Part A*, 1994, **50**, 2291.

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