Assessing the Degree of Partial Oxidation in One-dimensional Conducting Iodides

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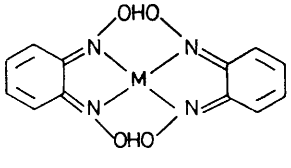
Summary The combination of resonance Raman and ^{129}I Mössbauer spectroscopy is an attractive tool for studying electron distribution in iodine-oxidised mixed-valence materials.

THE solid-state electron-transport properties of stacked planar inorganic and organic molecular systems are frequently enhanced by chemical oxidation.[1] In the case of square-planar transition metal complexes, halogen oxidation can produce highly (and anisotropically) conducting mixed-valence materials such as $K_2Pt(CN)_4Br_{0\cdot30}\cdot3H_2O$.[1,2] Any rational synthetic programme to expand the diversity and to control the properties of such compounds must be guided by a means of assaying the degree of oxidation. This is also true for any theoretical attempts to understand the physical properties.[1-3] In many cases the actual degree to which the stacked square-planar species have been oxidised, *i.e.*, the extent of electron transfer from donor to acceptor, remains a mystery. This is especially true of a number of iodine-containing materials[4] where frequently *X*-ray diffraction structures are non-existent or disordered, and where iodine could be present as I_3^-, I^-, or I_2. We demonstrate here that the combination of resonance Raman and ^{129}I Mössbauer spectroscopy represents a convenient tool for structure and oxidation state elucidation in such iodine-containing compounds. Though we give an inorganic compound as an example, the approach should be applicable to organic systems as well.



(1); M = Ni or Pd

Endres *et al.*[5] reported that iodine oxidation of bis(1,2-benzoquinone dioximato) (bqd) complexes of nickel or palladium (**1**) yielded crystalline materials of the stoicheiometry $(bqd)_2MI_n$, where $n = 0\cdot50$–$0\cdot70$. Since the chains of iodine atoms present in the lattice are disordered along the stacking direction, only a single, average I · · · I contact was observed in the *X*-ray structure,[6] and it was impossible unambiguously to infer the form(s) of the iodine present (the authors preferred the I_3^- formulation[5]). We have prepared the nickel complex as described in the literature,† and in contrast to the ambiguity of the diffraction data, the resonance Raman spectra (spinning samples, 6471, 5145, or 4880 Å excitation) clearly show the intense fundamental and overtone progression of I_3^- (Figure A).[7] The observation of the tri-iodide 'antisymmetric' stretch at 163 cm^{-1} indicates some distortion of the ion from idealised $D_{\infty h}$ symmetry.[7a] The presence of molecular I_2 (ν *ca.* 205–180 cm^{-1}), easily detectable by resonance Raman spectroscopy in such known compounds as $(\text{phenacetin})_2H^+I_3^-{\cdot}I_2$[8a] (*e.g.*, resonance-enhanced emissions at 187vs and 120s cm^{-1} with 5145 Å excitation) as well as $Et_4N^+I_3^-{\cdot}2I_2$[8b,d] and $2Cs^+(I_3^-)_2{\cdot}I_2$[8c,d], is unobserved in the present case. These conclusions are supported by complementary ^{129}I Mössbauer studies (Figure B). The parameters obtained [I.S. e^2q (Q/h) = 1·52 (−1710), 1·13 (−1170), and −0·25 (−700) mm s^{-1} *vs.* ZnTe (MHz, ^{129}I)] are in good agreement with published data for I_3^-,[9,10] especially when distortion (unequal I–I bond lengths) is known to be present[4,9b] [*e.g.*, CsI_3, 1·15 (−1782), 0·12 (−1041), and −0·12 (−637)[11]]. At the present level of detection, the amount of I^- which could be present is <3% of the total I, and I_2 is <5%. Further refinement of these data is in progress. Thus, our results confirm the proposal of Endres *et al.*[5] and indicate that the iodine in this material is present predominantly as I_3^-. In terms of electronic structure, this means that the charge transferred from the donor to acceptor chain is $n/3$ electrons per $(bqd)_2Ni$ unit. The potential of the Raman–Mössbauer structural technique to provide charge transfer information is clearly apparent and it is being presently applied to a number of other one-dimensional systems.

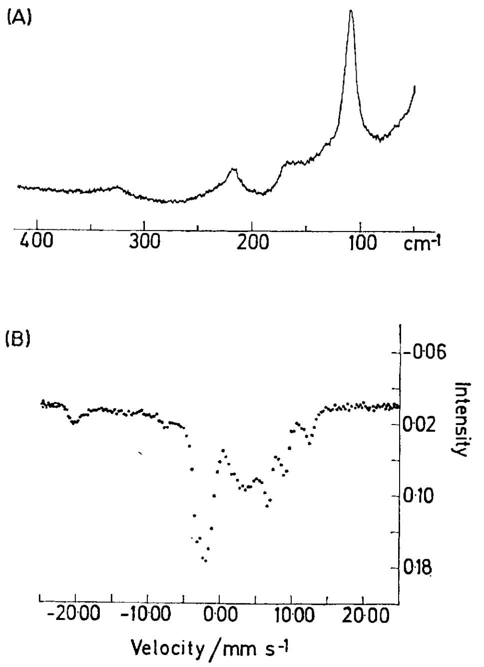


FIGURE. (A) Resonance Raman spectrum of $(bqd)_2NiI_{1\cdot 0}$ with 5145 Å Ar^+ excitation, and (B) ^{129}I Mössbauer spectrum of the above compound *vs.* ZnTe.

Added in proof: diffuse *X*-ray scattering measurements also suggest ahe presence of I_3^- in $(bqd)_2NiI_{0\cdot 5}$.[12]

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† Depending on the amount of iodine used and the oxidation conditions, it is possible to achieve a range of stoicheiometries which presumably reflect the filling of the various channels in the lattice[6] The data reported here appear to be general for *n* up to *ca.* 1·0.

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