Resonance Raman and Electronic Spectra of Mixed Valence Compounds with Ni(II)---X-Ni(IV) and Ni(II)---X-Pt(IV) Chains (X = Cl or Br)

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The resonance Raman and electronic spectra of compounds Ni(en)2X3, Ni(dapn)2X3 etc. and of compounds [Ni(en)2Pt(en)2X2][ClO4]4 (where X = Cl or Br) show that these are mixed valence compounds with a metal halide chain (en = 1,2-diaminoethane, dapn = 1,2-diaminopropane).

The pure nickel compounds were prepared as in ref. [29]. One should use anhydrous forms of starting materials, i.e., Ni(dapn)2Cl2 etc. It was found that Ni(dapn)2X3 are precipitated easier than Ni(en)2X3. The following method gave crystalline Ni(dapn)2X3 precipitates. A saturated solution of Ni(dapn)2X2 in methanol-ethanol 1:5 mixture was oxidised by passing N2-X2 gas mixture. Dark blue (X = Cl) or dark red (X = Br) solution* was obtained which precipitated small crystals after a few hours. The precipitate Ni(dapn)2X3 was filtrated, washed with methanol-ethanol (1:1) mixture, then with pure ethanol, carbon tetrachloride and air dried. Small crystals with a copper (X = Cl) or copper-gold (X = Br) luster were stable in dry atmosphere. Elemental analysis for Ni(dapn)2Br3, which is a new compound, gave the following results.

Analysis: C8H25NiBr3


Found C 15.08 H 4.64 Ni 13.31.

C 16.30 H 4.40.

Using concentrated solutions of Ni(en)2X2 or Ni(dapn)2X2 in methanol and passing N2-X2 gas one can obtain thin shining deposits on the vessel wall or on the quartz-cell wall suitable for optical measurements. The same method was applied for preparation of Ni(en)2Cl3 and Ni(en)2Br3. Starting from Ni(ClO4)2 the compound Ni(dapn)2[ClO4]2 was prepared. Solution of this compound in methanol gave shining crystals of Ni(dapn)2X2ClO4 in a few hours after passing N2-X2 gas mixture.

* Perhaps the dark solution contains a large portion of Ni(dapn)2X4.

* Reprint requests to Dr. G. C. Papavassiliou.

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* Perhaps the dark solution contains a large portion of Xi(dapn)2X4.

The electronic spectra of this kind of solids show strong size effects [21–25]. These compounds are insulators or semiconductors. The gap frequency is (which is twice the activation energy) found by optical measurements [21, 25] in a good agreement with that obtained from electrical conductivity measurements [26, 27]. In [Pd(en)2]2Pd(en)2Br2] (ClO4)4 for example the corresponding values of the gap frequency are 0.967 [21] and 0.98 eV [26].

In ref. [28] was reported that the compound Ni(en)2Cl3 (en = 1,2-diaminoethane) is a low-spin Ni(III) complex while the compound Ni(dapn)2Cl3 (dapn = pn = 1,2-diaminopropane) is a Ni(II)-Ni(IV) mixed valence complex. In this paper we report the resonance Raman and electronic spectra of Ni(en)2Cl3, Ni(dapn)2Cl3, Ni(en)2Br3 (see ref. [28, 29]) and show that these compounds are mixed valence compounds with a Ni(II)--X--Ni(IV) chain (X = Cl or Br). Moreover, we report the preparation and the spectra of some new compounds with Ni(II)--X--Ni(IV) and Ni(II)--X--Pt(IV) chains.

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* Perhaps the dark solution contains a large portion of Ni(dapn)2X4.
[Ni(en)$_2$Pt(en)$_2$X$_2$] (ClO$_4$)$_4$ compounds (X = Cl or Br) were prepared as following: To a solution of [Pt(en)$_2$Cl$_2$]Cl$_2$ (0.2 g) and NaClO$_4$ · H$_2$O (0.35 g) in water (10 ml) a solution of Ni(en)$_2$Cl$_2$ (0.11 g) in water (1 ml) was added. Immediately a reddish crystalline compound was precipitated. The precipitate was dissolved by warming the mixture at 95 °C and left for crystallization at room temperature. After a few hours long needle-shaped crystals of [Ni(en)$_2$Pt(en)$_2$Cl$_2$][ClO$_4$]$_4$ were collected, washed with cold water and air dried.

Analysis: C$_8$H$_{32}$N$_8$Cl$_4$O$_{16}$NiPt
Caled

The compound [Ni(en)$_2$Pt(en)$_2$Br$_2$][ClO$_4$]$_4$ was prepared by using equivalent amounts of [Pt(en)$_2$Br$_2$]Br$_2$ instead of [Pt(en)$_2$Cl$_2$]Cl$_2$ and Ni(en)$_2$Br$_2$ instead of Ni(en)$_2$Cl$_2$.

Analysis: C$_8$H$_{32}$N$_8$Cl$_4$Br$_2$O$_{16}$NiPt
Caled Ni 5.58 Pt 18.55.
Found Ni 5.54 Pt 18.50.

Raman spectra were recorded using a Jobin Yvon Ramanor model HG-2S spectrometer. Exciting radiation was provided by a Spectra-Physics argon and a Spectra-Physics helium-neon laser. The electronic absorption spectra were recorded with a Cary 17 D spectrophotometer.

Fig. 1. Resonance Raman spectra of Ni(dapn)$_2$Cl$_3$ (a), Ni(en)$_2$Cl$_3$ (b) [Ni(en)$_2$Pt(en)$_2$Cl$_2$] (ClO$_4$)$_4$ (c) observed with E//Z (c). Excitation $\lambda_1 = 454.5$ nm.

Fig. 1 shows the resonance Raman spectra of polycrystalline pellets of Ni(dapn)$_2$Cl$_3$ (a) and Ni(en)$_2$Cl$_3$ (b) and the spectrum of [Ni(en)$_2$Pt(en)$_2$Cl$_2$][ClO$_4$]$_4$ single crystal (c) observed with the wavenumber (E) of exciting light parallel to the needle-axis (Z). One can see that there are no considerable differences between the spectra (a) and (b) of Fig. 1. This means that, in contrast to the authors of ref. [28] and in accordance to that of the authors of ref. [29], both compounds Ni(dapn)$_2$Cl$_3$ and Ni(en)$_2$Cl$_3$ are mixed valence compounds with a Ni(II)...Cl...Ni(IV) chain. The peak at 263 cm$^{-1}$ is attributed to the fundamental stretching vibration of the Ni(II)...Cl...Ni(IV) chain. The peaks at 527, 793, 1055 cm$^{-1}$ are attributed to the first, second and third overtones respectively. The spectrum of [Ni(en)$_2$Pt(en)$_2$Cl$_2$][ClO$_4$]$_4$ is similar to that of [Pt(en)$_2$Pt(en)$_2$Cl$_2$][ClO$_4$]$_4$ [18] but as in the case of compounds with a Pd(II)...Cl...Pt(IV) chain [2, 18], the peaks occur at higher frequencies than those of [Pt(en)$_2$Pt(en)$_2$Cl$_2$][ClO$_4$]$_4$. Fig. 2 shows the Raman spectrum of a polycrystalline pellet of Ni(dapn)$_2$Br$_3$ (a) and the spectra of single crystals of [Ni(en)$_2$Pt(en)$_2$Br$_2$][ClO$_4$]$_4$ (b) and [Pt(en)$_2$Pt(en)$_2$Br$_2$][ClO$_4$]$_4$ (c) observed with E//Z. The spectrum of Fig. 2 (a) does not show any resonance enhancement. The reason is that the band in the electronic spectrum of Ni(dapn)$_2$Br$_3$ occurs at a very low frequency (see below) in comparison to the excitation frequency ($\omega_L = 15803$ cm$^{-1}$). Similar results were obtained for Ni(dapn)$_2$Br(ClO$_4$)$_2$ with $\omega_L = 15803$ cm$^{-1}$ and for [Pd(en)$_2$Pt(en)$_2$Br$_2$][ClO$_4$]$_4$ with $\omega_L = 22000$ cm$^{-1}$. The peaks in the spectrum of [Ni(en)$_2$Pt(en)$_2$Br$_2$][ClO$_4$]$_4$ (Fig. 2 b) occur at higher frequencies than those of [Pt(en)$_2$Pt(en)$_2$Br$_2$][ClO$_4$]$_4$ (Fig. 2 c).

The optical absorption spectra of nickel or nickel-platinum mixed valence compounds show strong size effects as in the case of pure platinum and palladium or platinum-palladium mixed valence compounds [16-25]. The optical absorption spectra of compounds with M...X...M...X...M...X...M...X...M...X...M.
chains are not superpositions of the spectra of their constituents [25]**. The band position and shape in the electronic spectra of thin deposits on quartz plates depends on the size of the particles. Thin deposits of Ni(dapn)$_2$Cl$_3$ or Ni(en)$_2$Cl$_3$ are copper-red in colour and become blue after rubbing with a soft paper. The colour changes due to the decreasing of the particle-sizes after rubbing. Fig. 3 shows the optical absorption spectra of Ni(dapn)$_2$Cl$_3$ and Ni(en)$_2$Cl$_3$ thin deposits on quartz plates before and after rubbing. One can see that Ni(en)$_2$Cl$_3$ shows the same spectra as Ni(dapn)$_2$Cl$_3$. This is in agreement with the observation of the authors of ref. [29], but in contrast to the observation of the authors of ref. [28]. The spectra reported in Fig. 2 ref. [28] correspond to a yellow-greenish compound which is obtained sometimes after chlorination of Ni(en)$_2$Cl$_2$. The presence of water favours the formation of the yellow-greenish product which may be a ligand deficient complex. Similar results were obtained after chlorination of Ni(tn)$_2$Cl$_2$ (tn = 1,3-diaminopropylamine). Thin deposits of Ni(dapn)$_2$Br$_3$ are copper-gold in colour. Their reflectance spectra show a broad band with a maximum at ca. 1450 nm. The deposits become green after rubbing with a soft paper and show an absorption peak at 905–nm (11040 cm$^{-1}$). The peaks in the electronic spectra of Ni(dapn)$_2$Br$_3$ and Ni(dapn)$_2$Br(ClO$_4$)$_2$ occur at lower frequencies than those of pure Pd- or Pt-compounds. This means that Ni compounds are more conducting than Pd- and Pt-compounds. Actually, we found that the d.c.-conductivity of Ni(dapn)$_2$Br$_3$ and Ni(dapn)$_2$Br(ClO$_4$)$_2$ (in pellets) is 10–50 times higher than that of [Pd(en)$_2$Pd(en)$_2$Br$_2$]ClO$_4$ [27]. The peaks in the optical absorption spectra of Ni(II)---X---Pt(IV) occur at higher frequencies than those of Pt(II)---X---Pt(IV).

The luminescence spectra of Ni(II)---Cl---Pt(IV) show a weak broad band at 650 nm (15384 cm$^{-1}$), while pure nickel compounds do not show any luminescence spectrum. Similar results have been obtained for Pd(II)---Cl---Pt(IV) and pure palladium compounds [25], while Pt(II)---Cl---Pt(IV) compounds show a strong luminescence peak at 1100 nm (9091 cm$^{-1}$) [25, 30].

** In ref. [25] was erroneously written that the spectra of these compounds are superpositions of the spectra of their constituents.
The similarity in the spectra of nickel mixed valence compounds with those of Pt- and Pd-compounds shows that the compounds described above have the formula \[\text{Ni}(\text{L-L})_2\text{M}(\text{L-L})_2\text{X}_2\text{Y}_4\] (where \(\text{M} = \text{Ni}\) or \(\text{Pt}\), \(\text{L-L} = 1,2\)-diamine, \(\text{X} = \text{Cl}\) or \(\text{Br}\) and \(\text{Y} = \text{Cl}, \text{Br}\) or \(\text{ClO}_4\)) with a \(\text{Ni(II)}\cdots\text{X}\cdots\text{M(IV)}\) chain.