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The Single Crystal Polarised Electronic Spectrum of All-trans Ni(as-N,N-dimethylethylenediamine)$_2$(trichloroacetate)$_2$ at 10 K

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We have recently reported the single crystal electronic spectra of a series of *trans* tetragonal nickel(II) complexes including that of the Ni(s-N,N'-dimethylethylenediamine)$_2$(trichloroacetate)$_2$ [1]. It was of interest to compare the spectrum of this symmetric diamine (s-Me$_2$en) species with that of the species prepared from the corresponding asymmetric diamine, as-N,N-dimethylethylenediamine (as-Me$_2$en). Previous X-ray data on a related complex of as-Me$_2$en [2], would lead one to believe that the Ni–N bond lengths should differ by about 8 pm, with the bond to the N(CH$_3$)$_2$ group being the longer. It was of especial interest to learn how this would be reflected in the spectrum of the complex, and to what extent it would influence the parameters derived.

Experimental

Single crystal polarised spectra were obtained at 10 K using a Cary 14 spectrometer, and a Displex cryogenic refrigerator, according to previously described conditions [1]. Data for the complex Ni(s-Me$_2$en)$_2$(trichloroacetate)$_2$ were abstracted from ref. [1]. However the single crystal spectrum is reproduced here for the first time. The complex Ni(as-Me$_2$en)$_2$(trichloroacetate)$_2$ was prepared according to Goodgame and Venanzi [3], and analysed satisfactorily for nickel. Calc. Ni, 10.48. Found Ni, 10.5%.

Results and Discussion

The structure of the title complex has not been investigated by X-ray techniques. However, we propose that it contains the all-*trans* configuration shown in (I). This conclusion is based upon several considerations arising from comparison of its single crystal spectrum with that of the symmetric diamine complex, see Fig. 1. The intensities of the bands decreased significantly on cooling the sample from room temperature to 10 K indicating vibronic selection rules and presumably an effective centre of symmetry. A *cis* configuration therefore seems

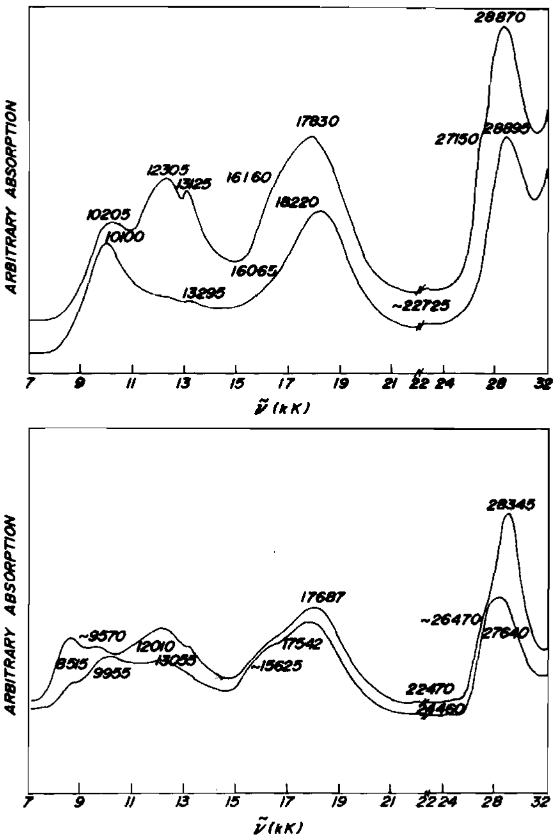
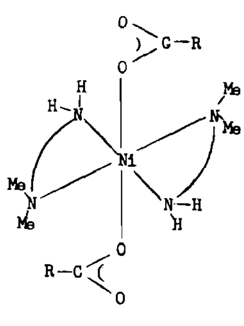
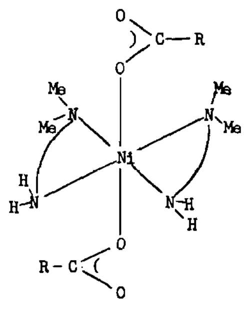


Fig. 1. (Upper) The single crystal spectrum of Ni(s-Me$_2$en)$_2$-(trichloroacetate)$_2$ at 10 K. (Lower) The single crystal spectrum of Ni(as-Me$_2$en)$_2$(trichloroacetate)$_2$ at 10 K. Two orthogonal polarisations are shown in each case. The narrow feature near 13000 cm^{-1} in each spectrum is a spin triplet–singlet transition.



(I)



(II)

improbable [4]. Moreover the details of the spectrum differ from those we have recently described to characterise *cis* nickel(II) complexes [4]. The two *trans* possibilities, (I) and (II), are readily distinguishable by their electronic spectra. Thus (II) should display 'Intermediate Symmetry' [5, 6], since it possesses pseudo D_{4h} symmetry (neglecting the carbon backbone). We could anticipate a spectrum generally similar to that of the symmetric diamine complex. The lowest lying orbital triplet, T_2, should split into two bands $^3B_2$ + ^3E. However, as is clearly shown in Fig. 1, the degeneracy of the lowest orbital triplet is completely lifted leading to the observation of three bands lying between 8000–15000 cm^{-1}. This is spectacularly evident when comparison is made with the symmetric diamine complex (Fig. 1). Above 15000 cm^{-1}, the spectra of the two complexes are very similar indeed, further supporting a gross similarity in structure.

Thus the evidence clearly supports structure (I). It is certainly relevant that a crystal structure of Cu(as-Me$_2$en)$_2$(hexafluoropentanedionate) [2] shows the all-*trans* configuration.

The complex (I) belongs to the point group C_{2v}(I) in the classification of reference [6] (or $C_{2v}\sigma_v$ according to ref. [7]). This complex (I) does not exhibit 'intermediate symmetry'. It has generally been observed that a distortion from octahedral structure reveals itself primarily in a splitting of the lowest lying spin allowed excited state and is less evident in higher excited states [8, 9]. This is a classical example of such a case.

We now turn to analyse this spectrum in terms of the Normalised Spherical Harmonic Hamiltonian (NSH) [6] and the Orbital Angular Overlap [10] models.

The appropriate Hamiltonian (NSH) in C_{2v}(I) symmetry is: [6]

$$\begin{aligned}\mathcal{H} = \mathrm{DQ}|A_{1g}O(i)|^{4}_{O_h} + \mathrm{DS}|E_gO(\theta)|^{2}_{O_h} &+ \\ + \mathrm{DT}|E_gO(\theta)|^{4}_{O_h} + \mathrm{DU}|E_g2+(\epsilon)|^{2}_{O_h} &+ \\ + \mathrm{DV}|E_g2+(\epsilon)|^{4}_{O_h}&\end{aligned}$$

The matrix elements for this problem are shown in Table X of ref. [6]. Further it is easy to demonstrate [4, 6, 10, 11] the following relationships between the NSH and OAM models (assuming the π OAM parameters are zero for the diamine):

$$\mathrm{DQ} = (\sqrt{21}/5)\{3\sigma_O + 3\sigma_N + 3\sigma_{N'} - 4\pi_O\}$$

$$\mathrm{DS} = (2\sigma_O + 2\pi_O) - (\sigma_N + \sigma_{N'})$$

$$\mathrm{DT} = (\sqrt{15}/5)\{3\sigma_O - 1.5(\sigma_N + \sigma_{N'}) - 4\pi_O\}$$

$$\mathrm{DU} = \sqrt{6}(\sigma_N - \sigma_{N'})$$

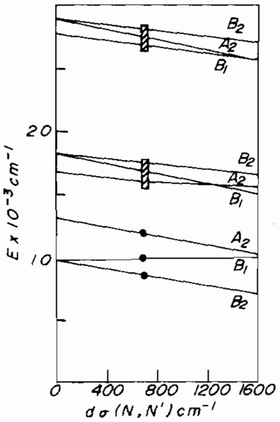


Fig. 2. Energy levels for d^8 in C_{2v}(I). The diagram portrays energy *versus* $d\sigma(N,N')$, the difference in σ anti-bonding parameter between the unhindered and hindered nitrogen donor atoms of the diamine ligand. The energy levels assume σ_N = 4400, σ_O = 2800, π_O = 400, and B = 875 cm^{-1}. A most acceptable fit to the spectrum of Ni(as-Me$_2$en)$_2$(trichloroacetate)$_2$ is shown in the figure at $d\sigma(N,N')$ = 700 cm^{-1}, *i.e.* $\sigma_{N'}$ = 3700 cm^{-1}. The appropriate NSH parameters are DQ = 28504, DS = –1700, DT = –4144, DU = 1715, and DV = –1992 cm^{-1}. With these parameters the calculated spin triplet energies are (rounded off): 8600 (B_2), 9950 (B_1) 11900 (A_2), 16100 (A_2), 16800 (B_1), 17600 (B_2), 26900 (A_2), 27600 (B_1) and 28300 (B_2) cm^{-1}. For comparison purposes the parameters for the symmetric diamine complex Ni(s-Me$_2$en)$_2$(trichloroacetate)$_2$ are σ_N = 4100, σ_O = 2425, π_O = –215, DQ = 30007, DS = –3787 and DT = –3234 cm^{-1}.

$$\mathrm{DV} = -(9/\sqrt{10})(\sigma_N - \sigma_{N'})$$

where σ_N and $\sigma_{N'}$ are the σ anti-bonding OAM parameters for the unhindered (NH_2) and hindered ($N(CH_3)_2$) donor atoms of the diamine ligand respectively, and σ_O and π_O are the σ and π OAM parameters for the trichloroacetate (TCA) ligand.

In Fig. 2 we use Hamiltonian (1) to show how the energy levels of a d^8 ion in a C_{2v} (I) environment vary as a function of $d\sigma$ (N,N'), the difference in σ antibonding between the NH_2 and $N(CH_3)_2$ ligating atoms of the diamine. The values of the Racah parameter B, and the OAM parameters σ_O (TCA) and σ_N (NH_2) were initially chosen according to previous experience [1, 12], the calculation was iterated around these values to achieve an acceptable fit. Experimental band energies are located on Fig. 2 at $d\sigma(N,N') \sim 700$ cm^{-1}.

Several interesting conclusions may be drawn after noting that a zero value of $d\sigma(N,N')$ corresponds to a pseudo-D_{4h} solution.

i) Indeed the splitting of the lowest lying orbital triplet state is a more sensitive function of $d\sigma$ (N,N') than are the splittings of the higher excited orbital triplets.

ii) The σ_N (NH_2) value (4400 cm^{-1}) falls well within the range anticipated for an unhindered amine–nickel bond [1, 12].

iii) The σ_O (TCA) value (2800 cm^{-1}) is in the same region as observed previously with haloacetate complexes of nickel(II), and π_O (400 cm^{-1}) is small, as anticipated [1, 12].

iv) A value of σ_N ($N(CH_3)_2$) of 3700 cm^{-1} is necessary to reproduce the spectrum. This does not seem out of line with the unhindered Ni–N value when the presumed 8 pm elongation is considered.

v) It is indeed possible to obtain a most satisfactory fit to the observed spectrum simply by accommodating a smaller value of σ_N for the hindered nitrogen atom and maintaining all other OAM parameters roughly unchanged from their anticipated values. This is a particularly nice example of the transferability of OAM parameters from one system (with care) to another [13].

We are currently investigating other all-*trans* $MN_2X_2Y_2$ species. In a recent vibrational analysis of nitrito complexes we reported the electronic spectrum of all-*trans* Ni(as-Me_2en)$_2$(ONO)$_2$ which also exhibits splitting of the lowest orbital triplet into three well defined components [14].

Acknowledgements

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11 The haloacetate is assumed to be orthoaxial, with a single π parameter, and all angles around the nickel atom are assumed to be 90°.

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13 There is a small family of solutions to this problem. Individual radial parameters may vary ±100 cm^{-1} without seriously vitiating the fit to the spectrum. B may vary ±25 cm^{-1}.
However note that the transition energy to the $^3A_2$ level is equal to 10 Dq (in-plane field) in the D_{4h} limit. Its dependence upon other parameters in this C_{2v} (I) problem is slight. Therefore 10 Dq ≅ 12000 cm^{-1} establishing the average in-plane σ_N value at ~4000 cm^{-1}. The splitting of the limiting E states in D_{4h} symmetry is determined primarily by $d\sigma(N,N')$.

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