Optical Resolution and Circular Dichroism Spectrum of a Complex containing Nickel(IV)

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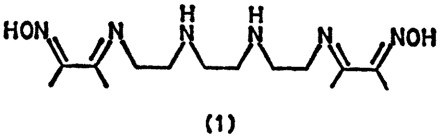
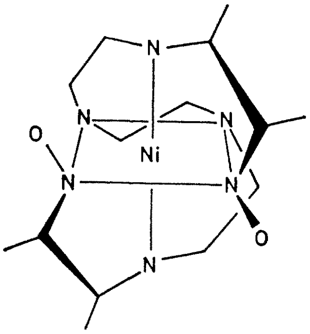
Summary The first optical resolution and circular dichroism spectrum of a complex containing nickel(IV) is reported.

VERY few compounds of Ni^{IV} have been reported[1] and, despite having the low-spin d^6 electron configuration in common with Co^{III}, Pd^{IV}, and Pt^{IV}, no complex of Ni^{IV} has been resolved into optical isomers. The sexidentate ligand 3,14-dimethyl-4,7,10,13-tetra-azahexadeca-3,13-diene-2,15-dione dioxime, H_2L, (**1**) readily forms[2] octahedral complexes with Co^{III}, Ni^{II}, and Ni^{IV}. Models suggest that only one of the possible geometric isomers is likely to be formed and this has been confirmed[3] for the Co^{III} complex by crystal structure analysis.

Chromatography of NiL^{2+} on SP Sephadex cation exchange resin confirms that, in this case also, only one geometric isomer is formed and we have succeeded in resolving this into optical isomers by elution with potassium (+)-antimonyl tartrate solution (0·025 mol l^{-1}). The c.d. spectrum of the first-eluted isomer of NiL^{2+} (**2**) (as the perchlorate salt) is shown in the Figure. The complex is optically stable, as expected for a low-spin d^6 ion, and slowly decomposed (over several weeks at 5 °C in aqueous solution) without racemisation. The Ni^{II} complex, on the



(1)



(2)

other hand, is labile; no optical activity is detected in a freshly reduced solution prepared from the resolved NiL^{2+}.

The c.d. spectrum shows a clear exciton couplet in the region of the first ligand transition. This is caused by the interaction of the two long-axis (parallel to the C–C bond) polarised transitions of the di-imine groups of the ligand and allows us to assign to the first-eluted isomer the absolute configuration shown in (**2**). The two absorption bands in the visible region at 20·0 and 23·25 × 10^3 cm^{-1} have been assigned[1] as ligand-to-metal charge-transfer transitions. This is supported by the value of their dissymmetry factors, $\Delta\epsilon/\epsilon$ (*ca.* 3 × 10^{-3}), which are similar to those for the well-established metal-to-ligand charge-transfer transitions of the di-imine complexes of Fe^{II} [4] and Ru^{II}.[5]

The complex is a good oxidising agent (E^0 0·94 V), oxidising many organic substrates (*e.g.* ascorbic acid, cysteine) smoothly and rapidly,[6] and has potential as an asymmetric oxidant. Preliminary studies show that L-(+)-cysteine is oxidised at least 50% more rapidly by the first-eluted isomer of NiL^{2+} than by its enantiomer.

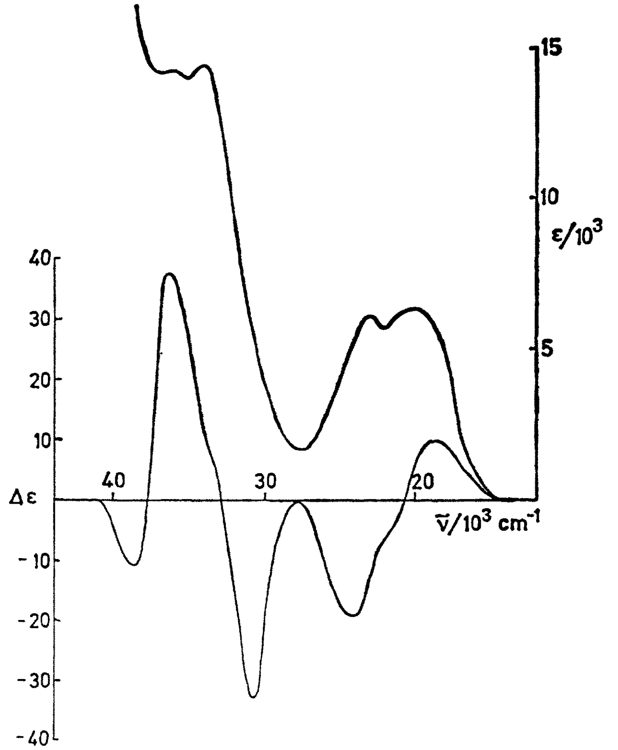


FIGURE. Absorption (upper curve) and circular dichroism (lower curve) spectrum of a 7 × 10^{-5} mol l^{-1} aqueous solution of $NiL(ClO_4)_2$.

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