The new bimetallic copper(II) complexes Cu[M(OR)₆]₂ exhibit a pronounced peak (g₁ = 2.10) and a broad and shallow peak (g₂ = 2.38), characteristic of axially distorted octahedral copper(II) complexes in which the unpaired electron is present in the dₓᵧ orbital.

Acknowledgements

We wish to thank Dr. S. Mitra, Tata Institute of Fundamental Research, Bombay (India) for providing facilities to record e.s.r. spectra and magnetic susceptibility measurements. One of the authors (R.K.D.) acknowledges the award of JRF in a DST project.

References


(Received July 11th, 1985)

The two trans-[NiL₂(NCS)₂] (L = N,N-dimethyl-1,3-propanediamine) Isomers in the Solid State and in Solution

Goutam De and Nirmalendu Ray Chaudhuri*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India

Summary

Two complex trans-[NiL₂(NCS)₂] (L = N,N-dimethyl-1,3-propanediamine) synthesised from solution in two isomeric forms (1) and (2), exhibit similar colours, magnetic moments and electronic spectra, but differ in their i.r. spectra and x-ray powder diffraction patterns. We suggest they possess trans-chair-chair and cis-chair-chair chelate conformations, respectively. Complexes (1)→(2) isomerise (temperature range 382–397.5 K; ΔH = 5.12 kJ mol⁻¹) in the solid state. Isomer (2) is converted into isomer (1) upon recrystallisation from chloroform. The trans-[NiL₂(NCSe)₂] complex does not isomerise upon heating. The compound [NiL(NCS)₂], prepared by thermal decomposition of [NiL₂(NCS)₂], possesses octahedral polymeric structure in which the diamine is chelated and all the thiocyanate groups are bridging.

Introduction

Problems relating to the phenomenon of structural change in coordination complexes in the solid state have been studied by various workers. Very recently, we reported some novel solid state reactions and phase transition phenomena associated with diamine complexes of nickel(II). These phase transitions were ascribed to conformational changes occurring in five- or six-membered chelate ring systems. From these studies we concluded that the diamine, which forms six-membered chelate rings with nickel thiocyanate, is capable of isomerising in the solid state. Studies of Ni(SeCN)₂ with this type of diamine could well be of interest and in this context, temperature dependent phase transitions as well as decompositions of N,N-dimethyl-1,3-propanediamine (L) complexes of NiX₂ (X = SCN and SeCN) are relevant.

Experimental

Trans-di-thiocyanatobis(N,N-dimethyl 1,3-propanediammine)nickel(II) (1)

A solution of diamine (L) (2 mmol) in EtOH (2 cm³) cooled to ~15°C was added dropwise to a similarly cooled EtOH (15 cm³) solution of Ni(SCN)₂·0.5H₂O (1 mmol), with stirring. The shiny fine crystalline compound separated from the resulting blue solution was removed by filtration, washed with EtOH and air dried. (Found: C, 37.9; H, 7.7; N, 22.2; Ni, 15.4. C₁₂H₂₈N₆S₂Ni calcd.: C, 38.0; H, 7.4; N, 22.2; Ni, 15.5%.)

Trans-di-thiocyanatobis(N,N-dimethyl 1,3-propanediammine)nickel(II) (2)

Diamine (3 mmol) was added to Ni(SCN)₂ (1 mmol) dissolved in EtOH at 30°C and the shiny blue crystals which separ-
isomers implies the presence of an identical [NiNr] geometrical as well as structural isomerism. The similarity of two isomers prove that the NCS groups are ligated each other, and nullify simultaneously the probabilities of v(CS) (5, 6) bands in i.r. spectra (Figure 1, Table 1) of the effect of the diamine (4) and the appearance of similar v(CN) vibrations. The strong

Results and Discussion

Preparation of (1) from (2). Complex (2) (1 g) was dissolved in CHCl3 (30 cm3) and the solution was evaporated to 3/4 of its vol. in a vacuum desiccator. The shiny crystals which separated were filtered off and air dried.

** Trans-di-isoselenocyanatobis(N,N-dimethyl 1,3-propanediamine)nickel(II)**

KSeCN (2–3 mmol) was added to NiCl2 · 6 H2O (1 mmol) dissolved in EtOH. The excess of KSeCN and KCl was removed by filtration and the filtrate containing NiI(SeCN)2 was transferred to a beaker containing diamine (2–3 mmol). Immediately, blue shiny crystals separated. These were filtered off, washed with EtOH, and air dried. (Found: C, 30.4; H, 6.1; N, 17.7; Ni, 12.5. C21H28N6Se2Ni calc.: C, 30.5; H, 5.9; N, 17.8; Ni 12.4%.)

** Di-isothiocyanatobis(N,N-dimethyl 1,3-propanediamine)nickel(II)**

This complex was prepared by heating (1) or (2) to 170°C (heating rate, 5 °C min−1) and then cooling the sample to room temperature in a N2 atmosphere. This cycle was repeated (usually 4–5 times) until the t.g. curve shows constant weight in the 130–170°C range. (Found: C, 27.0; H, 5.5; N, 21.1; Ni, 22.1. C21H28N6Se2Ni calc.: C, 27.2; H, 5.3; N, 21.2; Ni, 22.2%.)

Reagents

A. R. grade chemicals were used. N,N-dimethyl 1,3-propandiamine (L), obtained from Fluka AG, was used without further purification.

Equipment and procedure

The apparatus employed for recording the spectral, magnetic, x-ray powder diffraction and thermal data were reported previously.[5]

Results and Discussion

We have synthesised two isomers (1) and (2) of [NiL2(NCS)2] from solution by varying experimental procedures. The strong trans effect[5] of the NCS group, the steric effect of the diamine[9] and the appearance of similar ν(CN) and ν(CS)[6, 8] bands in i.r. spectra (Figure 1, Table 1) of the two isomers prove that the NCS groups are ligated trans to each other, and nullify simultaneously the probabilities of geometrical as well as structural isomerism. The similarity of the magnetic and electronic spectral data (Table 2) of the two isomers implies the presence of an identical [NiN6] chromophore in both. On the other hand, the dissimilarity of the i.r. spectra of the complexes as well as x-ray powder diffraction patterns, (Table 3) indicate that these two isomers probably differ only in their chelate ring conformations. For the six-membered chelate ring system in trans-[M(pd)2] (pd = 1,3-propanediamine)[7] a symmetrical chair conformation is preferred, because interactions with the apical ligands, (a), are relieved by a general flattening of the ring. Thus two forms of trans-[NiL2(NCS)2] may exist: (i) trans-chair-chair and (ii) cis-chair-chair [Structure (i) and (ii)]. Isomer (1) should have a trans-chair-chair conformation as it is energetically more favourable and symmetrical (S₄) than the (2) isomer (C₄); isomer (1) transforms to isomer (2)** upon heating 382–397.5 K; AH*** = +5.12 kJmol−1. The observed energy difference****, 5.12 kJmol−1, appears low by comparison with the theoretically calculated energy difference between the two forms of M(pd)2 (6.7 kJmol−1), evaluated by Geue and Snow[8]. This fact might be due to the presence of N-methyl substituents on diamine, since it is clear that M–N bond distance (methyl substituted nitrogen N') increases and, simultaneously, the N–M–N' angle decreases causing some distortion of the chair conformation of the six-membered chelates[7]. We only find i.r. spectral changes in the NH2 vibrational and C–N stretching mode[9] regions (Figure 1; Table 1). These changes are likely if we consider the spatial position of the two rings with respect to the nickel(II) ion and thiocyanate group. In isomer (2) the four nitrogen (NN'NN') atoms and one of the N'-methyl carbons remains almost in one plane, but the methyl group trans to the N'-methyl group makes an angle with this plane, thus affecting the N-H vibrations of the NH2 group. However, in isomer (1) the four nitrogen (NN'NN') atoms remain on the same plane and all four methyl groups remain either above or below it. As a result, the NH2, N-H vibrations experience an average interaction and thereby the number of i.r. active vibrations is less compared with (2). The C–N stretching vibration of (2) appear to split compared to (1), presumably as a result of the presence of a net C–N dipole moment which affects the C–N stretching modes. Splitting is observed compared to the C–N stretching modes of (1), where the individual C–N dipole moments cancel. These observations are commensurate with our propositions relating to isomers (1) and (2). It is interesting that although (2) is very stable in the solid state, when (2) is dissolved in CHCl3 (1) from the solution crystallises. Isomerisation taking place on solvation

---

** Considering the molecular model (taking NCS groups as an unit system).

** This species has identical x-ray powder pattern and i.r. spectral data to isomer (2), prepared from solution.

*** ΔH value is calculated from the d.s.e. curve (Figure 2). The enthalpy of melting of indium was used in calculating the enthalpy change associated with phase transition.

**** ΔH = ΔE is assumed, as ΔV = 0 for the solid state transformations.