

SPECTROSCOPIC AND ELECTRICAL CONDUCTIVITY STUDIES OF SOME METAL ACETYLACETONE COMPLEXES

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Abstract

Electrical conductivity, reflectivity and infrared spectra have been studied for some transition metal acetylacetonate complexes. All samples exhibit a semiconducting behaviour and the activation energy varies linearly with the number of d-electrons. All complexes carry some covalent character and the obtained data was analysed in terms of the ligand field theory.

Introduction

The detailed electronic structures and the nature of bonds of the chelate compounds of transition metal ions are still undetermined. Some authors [1] have applied the crystal field theory to these complexes and proposed that the ionic view point is capable of explaining some of their properties, e.g., magnetic susceptibility and spectra. Other workers have assumed that these compounds are completely covalent.

Nakamoto et al. [2-4] have investigated the infrared spectra of divalent and trivalent metals acetylacetonates to correlate the electronic structure of chelates with the calculated force constants. Also they have studied the relationship between force constants and thermodynamic data.

Vapour pressure-temperature relation was studied for a series of metal β -diketone chelates [5]. It was found that the degree of volatility is dependent on the molecular symmetry and polarity of the molecule.

The infrared spectra of different rare earth acetylacetonates have been investigated and normal coordinate treatments have been used [6].

Electrical conductivity have been studied for some chelates of chromometric acid with some transition metals [7]. All samples obey a semiconducting behaviour and the activation energy was found to be dependent on the number of d-electrons.

The aim of the present work is to shed light on the structure and nature of bonding in metallo-organic chelates. Optical observation technique is usually applied to investigate the symmetry, ligand field and degree of covalency of metal ligand bond [8,9].

Experimental

All chemicals used are of high purity. The samples were prepared by dissolving the appropriate metal salt in distilled water and buffered with sodium acetate. The buffered metal ion solution was added to acetylacetone in methanol with stirring. The mixture was heated briefly on hot plate, and after cooling crystals were separated out and dried in vacuo.

Reflection spectra of the powder samples were measured using Carl Zeiss PMQ 11 spectrophotometer in the region 300-2500 nm. The resistance of the samples, pressed in disk shape, was directly obtained using Keithly 616 C electrometer.

The infrared spectra were recorded using Perkin – Elmer 1430 recording IR spectrophotometer.

Electrical conductivity .

Fig. (1) shows the temperature dependence of conductivity for the investigated solid complexes. All samples exhibit a semiconducting behaviour where the conductivity increases by increasing the temperature. The values of activation energies ΔE_i in the high temperature region (intrinsic) are listed in table (1).

Table (1): Values of activation energies ΔE_i for metal complexes

Compound	ΔE_i (ev)
V-A	0.82
Fe-A	0.92
Co-A	1.1
Ni-A	1.25
Cu-A	1.32

In the case of iron and nickel chelates, two activation energies are observed. This behaviour is due to two different conduction mechanisms. At moderate temperatures we are dealing with an extrinsic semiconductor where conduction is due to the excitation of carriers from donor or acceptor localized levels to the conduction band. This is characterized by relatively low activation energy. On increasing temperature, the intrinsic region is reached, where the carriers are thermally activated from the valence band to the conduction band.

The dependence of activation energy ΔE_i on the number of d-electrons is shown in Fig. (2). A linear relation is obtained which indicates that d-electrons may contribute to the conduction process.

Beside the role of d-electrons, there are two other factors which affect the conduction mechanism : (i) The delocalization of π -electrons of the molecule (ii) The donating power of the methyl group (CH_3).

According to the configurational model [10], the transition metal ion tends to lie in one of the stable configurations d^0 , d^5 and d^{10} . When $3 < n < 5$ the tendency to attract electrons is the likely process. On the other hand when $5 < n < 10$ the opposite process takes place where the repulsion of external electrons is increased. The latter process will decrease the degree of delocalization and consequently increase the activation energy.

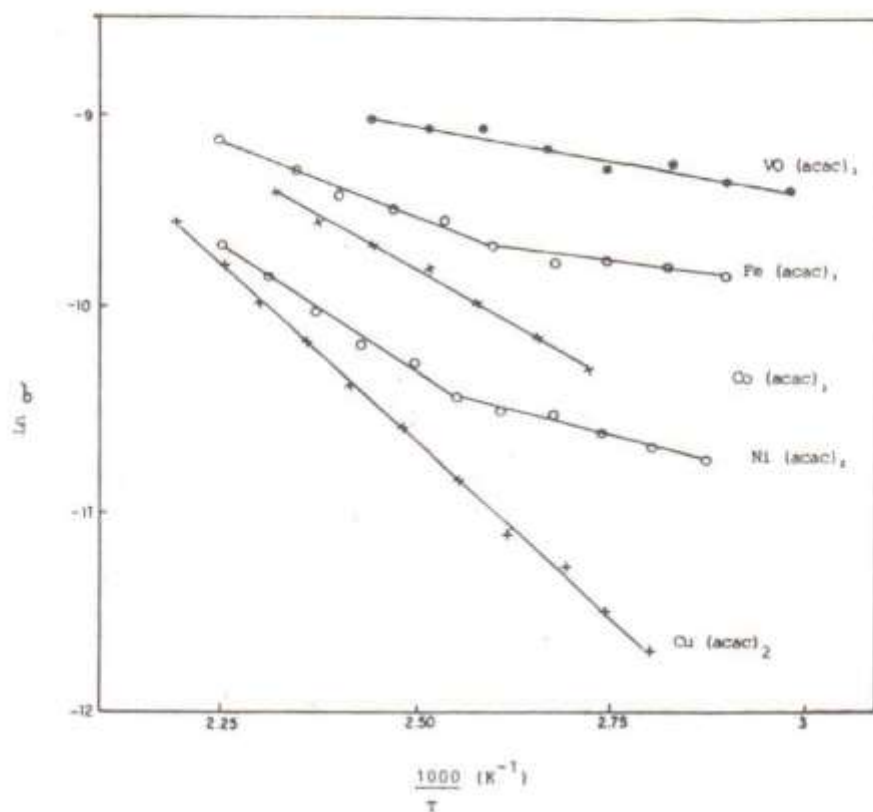


Fig. (1): Temperature dependence of conductivity for solid complexes.

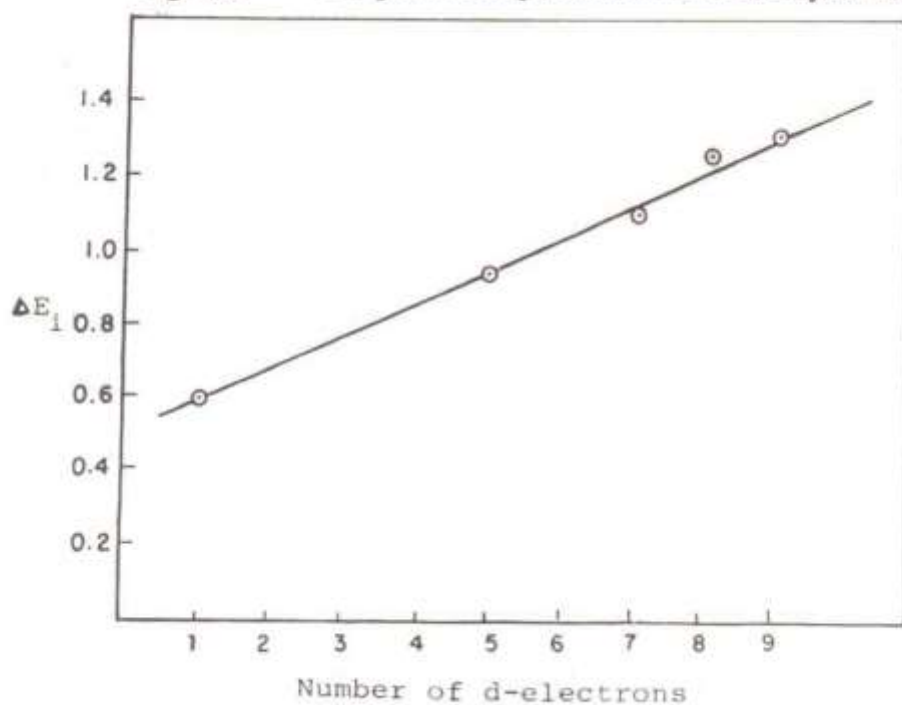


Fig. (2): Variation of activation energy ΔE_1 with d-electrons.

Moreover, the electron releasing properties of the methyl group (CH_3) should increase the electron density on the four ligand oxygen atoms. This will lead to an increase of the degree of delocalization of electrons and therefore the activation energy will be reduced. In the case of Fe (III), the donating power of ligand oxygens is greater, and in turn a more reduction in ΔE is expected. V(IV) has the lowest activation energy since it is easy to get d^0 configuration by losing the one d-electron. The sizes of the electron clouds about the metal and ligand atoms are certainly great enough to cause considerable overlap and thus exchange of electrons among these atoms. Accordingly, a considerable amount of covalent character is expected in the chemical bonds of such compounds.

The above results agree with the previously published data concerning heatstabilities of the acetyl-acetonates derived from a number of different metals. The trivalent iron was found to be quite unstable while the stability of Co(II) is slightly better. Ni (II) and Cu(II) were found to be the most stable of divalent transition metal acetylacetonates studied. In other words, the activation energy is directly proportional to the degree of heat stability for such compounds.

Optical Reflectance

Fig. (3) illustrates the reflectance spectrum for nickel chelate. Three well defined bands were observed which are characteristic of divalent nickel in octahedral symmetrical field. The 1st band was found at 1800 nm (5555 cm^{-1}) and was assigned as ν_1 due to ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition. The second band located at 900 nm (1111 cm^{-1}) was assigned as ν_2 due to ${}^3T_{1g} \leftarrow {}^3A_{2g}$ transition. The third high energy band ν_3 lies at about 550 nm (18181 cm^{-1}) and is due to ${}^3T_{1g}(\text{P}) \leftarrow {}^3A_{2g}$. These transitions were used to estimate the ligand field strength $10 Dq$ and Racah constant β . [12]. A value of 743 cm^{-1} was obtained for Racah constant which is less than that of the free ion value ($\beta_0 = 1041 \text{ cm}^{-1}$). This indicates that the nickel chelate carries some covalent character ($\beta/\beta_0 = 0.73$).

The reflectance spectrum of cobalt acetylacetonate is shown in Fig. (3). The asymmetric visible band at about 13300 cm^{-1} (ν_3) is typical of the spectra of octahedral cobalt (II) complexes and may be assigned due to ${}^4T_{1g}(P) \leftarrow {}^4A_{1g}$ transition. The shoulder on the high energy side (20619 cm^{-1}) being assigned to spin forbidden transition. The band located at about 5555 cm^{-1} is due to ${}^4T_{2g} \leftarrow {}^4T_{1g}$ transition (ν_1). The weak bands in the visible region at 6250 and 7300 cm^{-1} cannot be assigned to ${}^4A_{2g} \leftarrow {}^4T_{1g}$ transition (ν_2), since ν_2/ν_1 is always invariant at $2.1 - 2.2$.

On the other hand when organic ligands are involved, it is probable that the ${}^4A_{2g}$ transition cannot be observed where the tail of the ligand absorption being enough to obscure it. The last two bands may arise through low symmetry components to the ligand field, but is more likely to arise from spin forbidden transitions.

Making use of ν_1 and ν_3 , a values of 694 cm^{-1} and 608 cm^{-1} were obtained for Dq and β respectively with $\beta/\beta_0 = 0.63$. ($\beta_0 = 791\text{ cm}^{-1}$).

A comparison of the value of β/β_0 in both cases of cobalt and nickel chelates, reveals that the degree of covalency in cobalt complex is higher. In other words, the electron contribution to conduction is greater. This agrees well with the conductivity data where the activation energy for cobalt is less than that of the corresponding value for nickel.

Fig. (3) illustrated the reflectance spectrum for Cu(II) chelate. One broad band is observed in the visible region near 15800 cm^{-1} (632 nm). The spectrum indicates that copper is octahedrally coordinated and is subjected to considerable Jahn-Teller effect distortion. It is not possible to determine values for the interelectronic repulsion parameters since all d-d transitions take place within components of the same free ion term.

IR Spectra

The infrared spectra of the metal complexes were recorded in the frequency range $300-4000\text{ cm}^{-1}$. The IR spectra of some metal

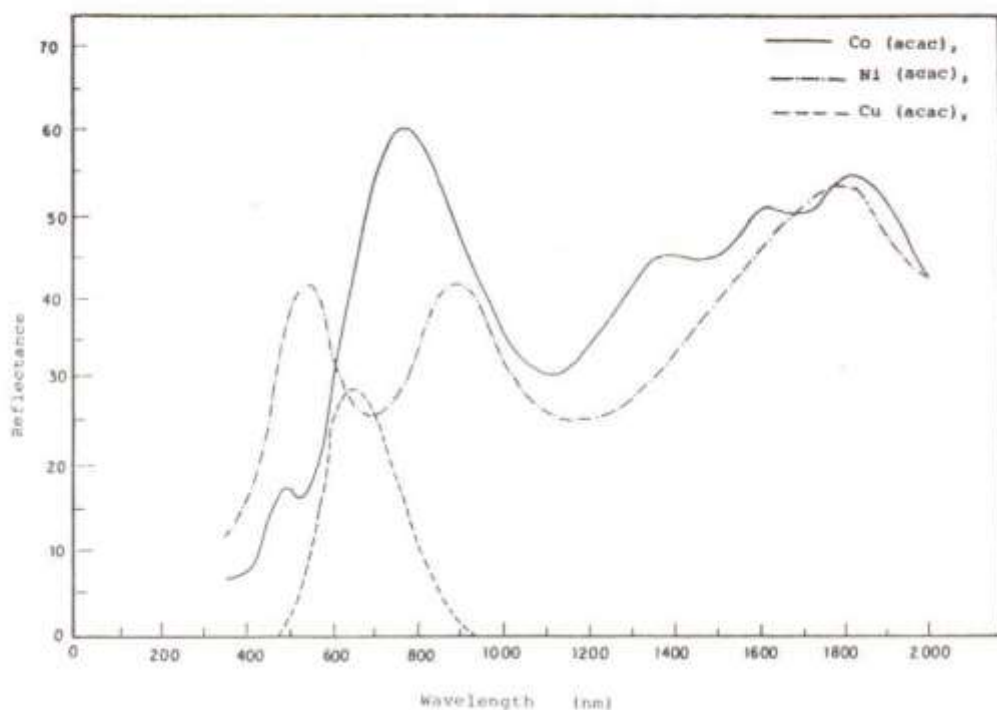


Fig. (3): Reflectance spectra of Cobalt, Nickel and Copper complexes.

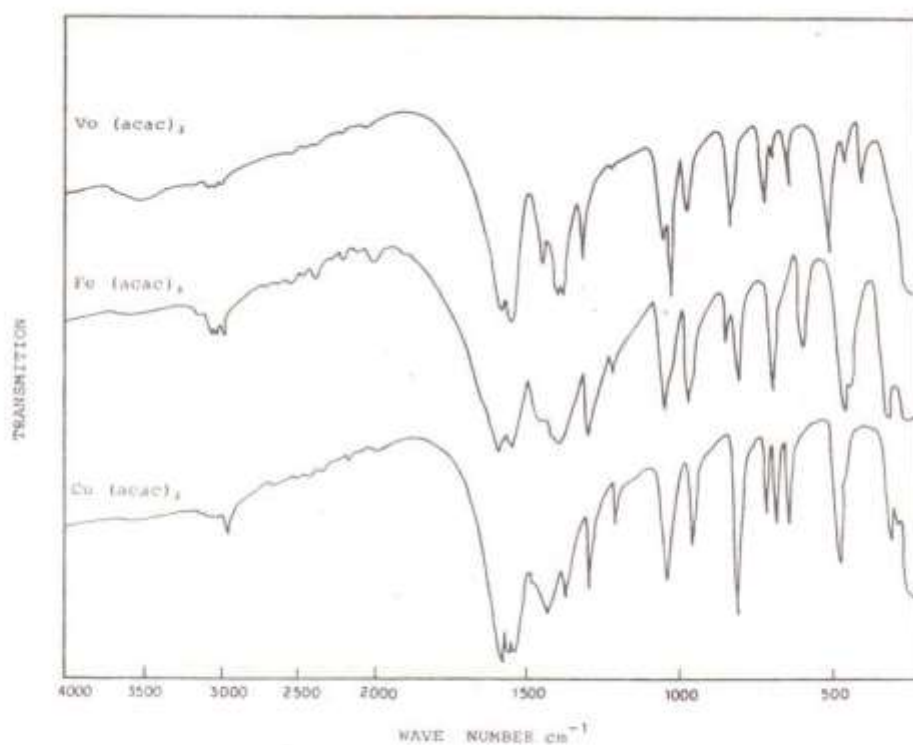


Fig. (4): IR Spectra of some metal acetylacetonates.

acetylacetonates are shown in fig. (4). From the investigation of the infrared spectra of these complexes, one could observe four absorption regions:

- The high frequency region around $\approx 3000\text{ cm}^{-1}$ includes absorption peaks attributed to symmetric stretching vibrations and these absorption features are not sensitive to the central metal ion.
- In the $1600\text{--}1500\text{ cm}^{-1}$ absorption range, all metal complexes have two strong absorption bands and the values of these frequencies are sensitive to metal ion. These two features are assigned to chelate ring vibrations to which the C=O and C=C bond stretching modes mainly contribute. $\text{Cu}(\text{acac})_2$ has one extra band in this region at 1557 cm^{-1} and is attributed to the combination band between two CH out-of-plane modes.
- Several absorption bands are observed in the region $1500\text{--}750\text{ cm}^{-1}$, some of these bands are sensitive to the central metal ion and some are insensitive to metal ion. Strong absorption peak is clearly resolved at 999 cm^{-1} and attributed to $\nu(\text{V}=\text{O})$ stretching vibration.
- In the region below 750 cm^{-1} , several groups of bands are observed. They are assigned to skeletal deformation vibrations and metal ligand stretching vibrations. All of them are more or less sensitive to the central metal ion.

The $\text{M}(\text{acac})_2$ complexes have a square planar structure of nearly D_{2h} molecular symmetry and the IR spectra are expected to obey the selection rules for the centrosymmetric point group and classified into the three symmetry species B_{1u} , B_{2u} and B_{3u} . While the $\text{Fe}(\text{acac})_3$ has octahedrally coordinated structure with D_3 symmetry. The structure of vanadyl acetylacetonate is tetragonal pyramidal, the vanadium atom being slightly displaced from the square plane of the ligand oxygen atoms. Assignments of observed frequencies are shown in table (2).

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