International Journal For Recent Developments in Science & Technology
2581-4575
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A Peer Reviewed Research Journal

Structural Studies of Transition Metal Complexes Using Spectroscopic and Thermal Methods

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Abstract

Transition metal complexes have a central role in contemporary inorganic chemistry since their electronic, magnetic and catalytic properties are closely related to their structure, which is closely connected with the coordination number, geometry, oxidation state and ligand field strength. These structural parameters can only be determined reliably with the use of a coordinated application of spectroscopic and thermal analytical methods, particularly in the case of compounds that do not form a single crystal. This paper summarizes the principles, instrumentation and interpretive systems of infrared, ultraviolet-visible, nuclear magnetic resonance and electron paramagnetic resonance spectroscopies and thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry to elucidate structure of transition metal complexes. The need to combine the complementary data sets for the determination of the denticity, geometry around the metal center, hydration and solvation states and thermal decomposition pathways of ligands is stressed. First-row transition metal Schiff base complexes and complexes containing a carboxylate are discussed as representative case studies to illustrate the integrated methodology. The review finds that none of the methods can provide an unambiguous structural assignment and that multiple methods are the most reliable means to obtain structural confidence without X-ray crystallographic data.

Keywords: Transition Metal Complexes; Spectroscopic Methods; Thermal Analysis; Coordination Chemistry; Schiff Base Complexes; Molecular Structure; Structural Characterization.

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1. Introduction

Transition metal complexes, that is, complexes of transition metals with partially filled d-subshells, have an extraordinarily rich variety of structure, colour and reactivity 1. Their structural diversity is responsible for their use in catalysis, bioinorganic chemistry, materials chemistry and medicinal chemistry. Structure determination of a newly synthesized complex (geometry at the metal center, the mode of ligand binding, the oxidation state of the metal and the presence of coordinated or lattice solvent) is a pre-requisite for understanding and prediction of the chemical behaviour of the complex 1.

Single-crystal X-ray diffraction is the ultimate approach to solving a structure, but in many cases, especially for poorly crystalline and amorphous materials, as well as for polymeric transition metal complexes, this approach is not possible. Chemists then have to use a convergent battery of spectroscopic and thermal methods to develop a self-consistent structural model in such cases. IR spectroscopy gives information on characteristic shifts of the vibrations on coordination 2, while UV-Vis spectroscopy gives information regarding the d-d and charge transfer transitions, which are characteristic of geometry and oxidation state 3; where applicable, NMR spectroscopy gives information on the ligand environment and symmetry 4, and electron paramagnetic resonance (EPR) spectroscopy gives information on the distribution of unpaired electrons in paramagnetic complexes 5, and thermal methods such as thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) give information on the loss of solvents, ligand decomposition and phase transitions as a function of temperature 6,7.

Each of these techniques is discussed here in turn, along with the type of structural information available and how, with the aid of other techniques, these can be used to make confident structural assignments in the absence of diffraction data (with representative examples).

2. Spectroscopic Methods

2.1 Infrared Spectroscopy

One of the most commonly used and inexpensive techniques used for investigation of the coordination environment of a transition metal complex is infrared spectroscopy.

Coordinating a ligand to a metal ion will alter the electron density of the functional groups in the ligand, and this change can be detected by a change in characteristic vibrational frequency for the functional group compared to the free ligand 2. These alterations (and not just the existence of a functional group) convey the structural information.

The carbonyl stretching (ν(C=O)) frequency is generally lowered when the carbonyl is coordinated due to the withdrawal of electron density towards the metal, weakening the C=O bond 2. The separation between the asymmetric and symmetric carboxylate stretches, $\Delta\nu = \nu\text{asym}(COO^-) - \nu\text{sym}(COO^-)$, will be diagnostic of the binding mode: a large Δν (greater than the free ionic value, typically > 200 cm^{-1}) will indicate monodentate coordination, a small Δν (below 110 cm^{-1}) will suggest bidentate chelating coordination, and an intermediate value will suggest bridging bidentate coordination 9. Azomethine ν(C=N) stretching frequency is a good indicator of the formation of Schiff base complexes, as it is lowered in frequency when the imine nitrogen is coordinated to the metal, due to donation of the imine nitrogen lone pair into the metal d-orbitals 2.

The low-frequency part of the infrared spectrum (ν < 600 cm^{-1}) is of special interest since it is rich in metal-ligand stretching and bending vibrations, such as ν(M–O), ν(M–N) and ν(M–Cl) which are not present in the free ligand spectrum, but only in the complex when the metal-ligand bond is formed 2. They are present, and so they are a direct, although not necessarily definitive, indication that coordination is present. Broad absorption bands in the 3200-3550 cm-1 range are generally assigned to the stretching vibrations of coordinated and lattice water and their presence or absence helps to distinguish hydrated from anhydrous species, which is then confirmed by thermal analysis 6.

2.2 Electronic (UV-Visible) Spectroscopy

Transition metal ions with partially filled d-orbitals have d-d transitions that can be excited by electronic absorption spectroscopy due to the lifting of the degeneracy of the d-orbitals caused by a surrounding ligand field 3. The number, position and intensity of the absorption bands formed depend on the symmetry of the ligand field and are thus informative of the coordination geometry (8).

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For first row transition metal complexes, there are usually two to three spin allowed d-d bands in the visible to near infrared region, whose energies can be used to determine the ligand field splitting parameter (10Dq or Δo) and Racah interelectronic repulsion parameter (B) by the application of a Tanabe-Sugano diagram. Within 3, octahedral complexes have molar absorptivities that are typically one or two orders of magnitude lower than tetrahedral complexes, which are not symmetrical.Within 3, the molar absorptivity of the d-d transitions are typically lower by one or two orders of magnitude for octahedral complexes, due to the lack of inversion symmetry, which relaxes the Laporte selection rule. D8 metal ions (Ni(II), Pd(II) and Pt(II) complexes) have typical band patterns, which are due to the transition between four different d-orbital energy levels 3,8.

At least d-d transitions, charge-transfer (CT) bands often also play a significant role in the UV region and sometimes even reach into the visible region 3. Ligand to metal charge transfer bands are very strong (molar absorptivity, greater than 1000 M-1cm-1, in complexes of higher oxidation state metals and easily oxidized donor atoms like S or O) and are caused by the transfer of electron density from filled ligand orbitals to empty or partially filled metal d-orbitals. The complexes with π-acceptor ligands, such as bipyridine or phenanthroline, however, have strong MLCT bands. The presence and strong intensity of the CT bands help to confirm the oxidation state of the metal centre and the electronic character of the ligand set 3.

Magnetic susceptibility measurements, which are sometimes reported with the electronic spectra, are also used to determine the number of unpaired electrons at the metal centre using the spin only formula: μeff = √[n(n+2)] Bohr magnetons, and in this way to distinguish, for instance, high spin from low spin for d8 systems 1,8.

2.3 NMR SPECTROSCOPY

The diamagnetic transition metal complexes are the most direct application of NMR spectroscopy, where the lack of unpaired electrons eliminates the large paramagnetic shift and line broadening typical of other complexes. 1H and 13C NMR spectra show shifts and coupling changes on coordination in diamagnetic d0, low spin d6 complexes (Co(III), Fe(II)) and d10 complexes, which provide information about the symmetry of the ligand and its binding mode. The loss of symmetry that is evident by

the presence of a single set of resonances in the free ligand and two inequivalent sets in the coordinated product suggests a particular chelation geometry 4.

NMR is informative for paramagnetic complexes, but is more complex to interpret. Line broadening of tens or even hundreds of parts per million and contact and pseudo-contact (dipolar) shifts due to interaction between unpaired electron spin density and nuclear spins can shift resonances by tens or hundreds of parts per million from diamagnetic references, 4. The size and direction of these paramagnetic shifts, if analyzed in a systematic fashion, can contain structural information about the spatial distribution of unpaired spin density, and in principle, about the distance and direction of the metal-ligand bond distances and angles, but this analysis is much more specialized than is the routine diamagnetic NMR analysis.

If NMR-active isotopes with suitable properties exist (e.g., 31P for phosphine, 19F for fluorinated, and metal nuclei, such as 59Co and 195Pt for heavy-metal complexes), the technique is also useful for these kinds of complexes; for these, the coupling constants (e.g., 1J(Pt–P)) can be directly diagnostic of trans influence of ligands and thus of overall geometry 4.

2.4 Electron Paramagnetic Resonance Spectroscopyuy

The electron paramagnetic resonance (EPR) spectroscopy is ideally designed to paramagnetic transition metal complexes and is able to observe transitions between electron spin states in the presence of an applied magnetic field 5. The technique provides the g-tensor, hyperfine coupling constants (with the metal nucleus and with coordinated ligand nuclei with non-zero spins) and, in the case of polynuclear systems, the zero-field splitting and exchange coupling parameters 5.

The symmetry of the obtained g-values from EPR is directly related to the symmetry of the ligand field 5. The g∥ and g⊥ values of the axial spectrum are typical of square pyramidal or tetragonally distorted octahedral geometries, whereas a fully rhombic spectrum (three separate g-values) is indicative of lower symmetry. The relative ordering g∥ > g⊥ > 2.0023 is diagnostic of a dx2−y2 ground state, typical of square planar, square pyramidal or tetragonally elongated octahedral, while the other ordering is typical of a dz2 ground state characteristic of trigonal bipyramidal geometry 5. This is further refined by hyperfine splitting from the copper nucleus (I = 3/2) and superhyperfine coupling from coordinated N donors (where resolved, this

will confirm metal-N bonds 5). EPR is thus an extremely useful tool when combined with electronic spectroscopy for mononuclear copper(II), vanadyl and manganese(II) complexes, and for the study of metal-centered radicals and mixed-valence complexes in polynuclear systems 5.

3. Thermal Analytical Methods

Thermal methods, in addition to spectroscopic data, provide information that cannot be obtained by spectrographic methods alone: numbers of molecules of water and/or solvent molecules associated with the complex, their mode of interaction (lattice versus coordinated), sequence and temperature ranges of the decomposition of the ligands, and the thermal stability and phase behavior of the solid residues 6.

3.1 Thermogravimetric Analysis (TGA)

TGA is a continuous technique that measures the loss of mass of a sample while it is heated at a constant rate under a specified gas atmosphere (usually a nitrogen, air or argon 7). The resulting thermogram, which is a plot of mass loss or its derivative (DTG) against temperature, is segmented into separate steps which correspond to individual decomposition and/or desolvation events 6,7. The percentage mass loss and the temperature range of each step are compared to the mass fraction of the loss of a particular structural unit (such as lattice water, coordinated water, or a specific part of the ligand) as determined from the proposed molecular formula 7.

A significant structural difference that TGA can be helpful in distinction is that between lattice (crystallization) water and coordinated water 7. The lattice water is normally lost at relatively low temperatures (usually below 120 °C) in a single, often slow step, because the hydrogen-bonding interactions holding the water to the crystal lattice are not as strong as those in the other water molecules. At higher temperatures, coordinated water is usually released as a more well-defined process, typically from 150 to 250 °C, due to the higher energy needed to break the metal-oxygen bond than breaking lattice hydrogen bonds 6,7. The observed mass loss temperature and percentage can then be correlated with the expectations to make confident assignment of the hydration state of a complex, to refine or confirm conclusions drawn from the broad O–H stretching band region of the infrared spectrum 2,7.

The further stages of mass loss in the higher temperature steps represent the successive breakdown of organic ligands, often leaving a metal oxide residue at temperatures above 500–600 °C 6. Elemental analysis 7 is supplemented by the mass of this final residue which is compared with that calculated for the corresponding metal oxide (e.g., NiO, CuO, Co3O4) for the metal content and for the stoichiometry of the original complex.

3.2 Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

Differential thermal analysis is a technique for measuring the temperature change between a sample and an inert reference while they are heated simultaneously, even when there is no measurable mass change and these events are not visible to TGA – such as crystalline phase transition, melting or the exothermic combustion of organic residue in an oxidising atmosphere 7. The principle can be extended to differential scanning calorimetry, which is directly able to measure the heat flow for each thermal event, giving enthalpies of dehydration, melting or decomposition in physically meaningful units (usually J/g or kJ/mol) 6,7.

Dehydration and desolvation processes are essentially always endothermic, and show a negative (or upwards, depending on convention) deviation from the DTA/DSC curve when they correspond to the mass loss step 7 in the TGA curve. In contrast, ligand decompositions and oxidative combustion tend to be very exothermic, especially under air or oxygen, since the organic framework is converted to CO2 and water. TGA combined with simultaneous DTA/DSC (simultaneous thermal analysis) can thus help to correlate each mass-loss event with its thermal signature and differentiate between simple desolvation and decomposition, and physical phase transition and chemical reaction 6,7.

In addition, the kinetic parameters of decomposition, such as activation energy and the order of the reaction can be determined from non-isothermal TGA data (obtained at several heating rates) by model-free approaches like the approaches of Kissinger, Ozawa-Flynn-Wall, and Coats-Redfern 10. These kinetic parameters, although not necessarily structural, are useful for comparisons when considering a series of related complexes where the changes in structure are consistent and the relative strength of metal-ligand and metal-solvent bonding is known, or when these changes are consistent with the Irving-Williams series.

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4. Integrated Structural Elucidation: Representative Case Studies

The true power of spectroscopic and thermal methods is that the individual methods are related to the same overall structure, the same consistent model, and that this model is derived independently from the two different sets of data. In this section, we will demonstrate the integrated approach using two classes of complexes that are typically studied in the first row of transition metals.

4.1 Schiff base complexes of Cu(II), Ni(II) and Co(II)

Some of the most widely researched transition metal complexes 1,2 are formed by the condensation of a primary amine with an aromatic aldehyde or ketone, usually containing in addition to the azomethine nitrogen, oxygen donors in the aromatic ring. The disappearance of the ν(O–H) of the free ligand and the shift of the ν(C=N) stretch to lower wavenumbers (usually 15–25 cm-1) in a representative tetradentate N2O2 Schiff base complex is a strong indication for deprotonation of the phenol and for coordination of the imine nitrogen and the phenolate oxygen donors to the metal center 2. In the low-frequency region (400-600 cm^{-1} and 400-450 cm^{-1}), new bands

The UV-Vis spectra of the Cu(II) complex generally show one broad band in the 550-650 nm region corresponding to the d-d band of the d9 copper complex, and a strong LMCT band in the near-UV region, which is characteristic of the phenolate to copper charge transfer transition 3,8. The EPR spectrum of the same complex recorded on a frozen solution, generally shows an axial spectrum with g∥ (ca. 2.20-2.25) significantly larger than g⊥ (ca. 2.05), and with resolved copper hyperfine coupling (A∥ typically 150-200 × 10^{-4} cm^{-1}) — parameters that, with the electronic

Isolated as the monohydrate, typical thermogravimetric analysis (TGA) of such complexes reveals an initial mass-loss step below 120 °C that is characteristic of the loss of one molecule of lattice water per formula unit followed at higher temperature by a series of overlapping exothermic mass-loss steps that are typical of oxidative decomposition of the Schiff base framework, to leave CuO as the stable residue above ca. 600 °C 6,7. The mass lost in the first step, when compared with the mass calculated on the basis of one water molecule per formula unit, is consistent with the hydration stoichiometry determined from the elemental analysis, and the fact that no distinct higher temperature dehydration step is observed (which would be expected near 200 °C, where coordinated water would be expected to dehydrate), further

supports the lattice, rather than coordinated, character of that water molecule 7, which is confirmed by the electronic and EPR data.

4.2 Carboxylate-Bridged Polynuclear Complexes

The separation in the carboxylate stretching region Δν in Section 2.1 9 is another example of the usefulness of infrared spectroscopy for diagnostic purposes in the complexation of metals by carboxylic acids. A Δν significantly below the free sodium carboxylate salt usually means that the bridging mode is bidentate, rather than monodentate, and can be confirmed by comparing with the expected CN from the electronic spectrum, and by comparison with any available magnetic susceptibility data; bridging carboxylates are commonly employed to provide antiferromagnetic exchange coupling between adjacent paramagnetic metal centres, causing μeff to deviate from the spin-only value of 5.

For such polynuclear carboxylate complexes, a typical thermal analysis decomposition profile is often observed: a low-temperature loss of coordinated/lattice solvent, an intermediate step characterized by the loss of some of the carboxylate ligands (in some cases accompanied by the appearance of a basic carboxylate or oxo-bridged intermediate, which can be detected as a plateau in the TGA curve), and a final high-temperature oxidation step to the metal oxide 6,7. The existence of a stable intermediate plateau as confirmed by holding the sample isothermally at the same temperature and seeing no further mass change is structurally informative in itself, since it is an indication of the existence of a true intermediate compound, and not just a continuum of decomposition 7.

5. Discussion – value of a multi-tech approach

The one thing that can be said about the case studies above is that each of the spectroscopic or thermal techniques provides evidence for a structural question that is not fully answered by the other techniques and that the more evidence of this type that is found the more confidence is placed in the proposed structure 1. Infrared spectroscopy is very sensitive to the immediate coordination environment of certain functional groups and offers only "indirect" information on the overall three dimensional geometry 2. While electronic spectroscopy is a good reporter of geometry and oxidation state in terms of ligand-field theory, it could be ambiguous in

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the presence of several plausible geometries giving rise to similar band patterns, especially in the case of distorted and intermediate geometries 3,8. However, the ambiguities can be clarified for paramagnetic systems by using EPR spectroscopy, which directly probes the symmetry of the singly occupied molecular orbital, but is unable to provide any information for diamagnetic complexes where NMR becomes the tool of choice 4,5. Thermal methods, last but not least, tackle questions which are generally beyond the scope of the other methods, and at the same time provide an independent check for the molecular formula on which all spectroscopic interpretation depends. 6,7

Technique	Primary Structural Information	Key Limitation
IR Spectroscopy	Ligand binding mode; presence of coordinated vs. lattice water; functional group identity	Indirect evidence of overall geometry; band overlap in complex ligands
UV-Vis / Electronic	Coordination geometry; oxidation state; ligand field strength (10Dq)	Ambiguity between similar geometries; requires known d-electron count
NMR Spectroscopy	Ligand symmetry and binding mode in diamagnetic complexes; solution structure	Limited to diamagnetic or fast-relaxing paramagnetic systems
EPR Spectroscopy	Ground-state symmetry; metal-ligand covalency; exchange coupling	Applicable only to paramagnetic complexes with suitable relaxation properties
TGA	Solvent/hydration content; decomposition stoichiometry; thermal stability	Cannot distinguish physical vs. chemical events without complementary DTA/DSC
DTA / DSC	Enthalpies of dehydration, melting, and decomposition; phase transitions	Requires mass-loss correlation (TGA) to assign event identity

Table 1. Summary of structural information and limitations of spectroscopic and thermal methods.

Even the combination of a number of spectroscopic and thermal methods is strong circumstantial evidence for structure, but no more, and in the absence of suitable crystals, single-crystal X-ray structure determination is the only way to arrive at unambiguous conclusions, particularly about bond lengths, bond angles, and space-group symmetry 1. The techniques reviewed here are therefore best seen as complementary to crystallography — essential when crystals are not available, and useful, even when they are, as there is often a meaningful difference between the solution and bulk powder behaviour as determined by NMR, EPR and thermal analysis, respectively, and the structure of the single-crystal 4,5,7.

6. Conclusion

Elucidation of structure of transition metal complexes without the use of diffraction quality crystals relies on the intelligent use of spectroscopic and thermal analytical information. Infrared spectroscopy gives technique-specific information on the nature of the ligands 2,9, electronic spectroscopy and magnetic susceptibility help determine the coordination geometry and the electronic configuration 3,8, while thermogravimetric analysis, differential thermal analysis and differential scanning calorimetry provide information on the composition, hydration state and thermal behavior which can only be guessed at by spectroscopy 6,7. While no single method works by itself, their mutual and complementary interpretation, illustrated in this case for Schiff base and carboxylate complexes of first-row transition metals, is powerful and general enough to be applied to all areas of coordination chemistry 1. This integrated method is expected to be further developed with the help of other complementary techniques, such as simultaneous thermal analysis (TGA) coupled with evolved gas analysis (EGA) (TGA-FTIR, TGA-MS) 10.

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