

Lanthanone Complexes of 2-Hydroxychalcones

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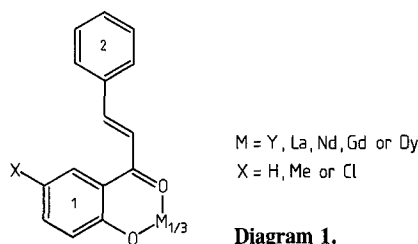
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Summary

A series of complexes of 2-hydroxychalcones with lanthanons having composition LnL_3 ($\text{Ln} = \text{Y, La, Nd, Gd, or Dy}$) were prepared and characterised by i.r. and electronic spectra, analytical and magnetic measurements. A symmetric arrangement of the three bidentate ligand molecules around the central lanthanide ion is suggested.

Introduction

Metal chelate complexes of acetylacetonates⁽¹⁾, salicylaldehyde⁽²⁾, β -hydroxy- α -naphthaldehyde⁽³⁾ and *o*-hydroxyaryl-carbonyl compounds^(4–6) have been subjected to extensive investigation, because of their potential use as laser materials^(7–9). However, no attempt has been made to study the effect of conjugation of an external double bond with the carbonyl group. We report the synthesis and characterisation of lanthanum(III), yttrium(III), neodymium(III), gadolinium(III) and dysprosium(III) complexes of 1-(2-hydroxyphenyl)-3-phenyl-2-propenone (1), 1-(2-hydroxy-5-methylphenyl)-3-phenyl-2-propenone (2) and 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-2-propenone (3).



Results and Discussion

The complexes are yellowish orange. All are sparingly soluble in both polar and non-polar solvents. Analytical data confirm the general formula LnL_3 . The lanthanum and yttrium complexes are diamagnetic, as expected. The magnetic moments of other metal ion complexes (Table 1), are not very different from those of the free metal ions, suggesting little perturbation of the metal 4f orbitals⁽¹⁰⁾.

A characteristic feature of the i.r. spectra of the complexes is the appearance of a prominent band in the region 470–490 cm^{-1} for all the chelates. From a comparison with the ligand spectra, we have tentatively assigned this to the M–O vibrational mode. Such bands have been observed in acetylacetonate⁽¹⁾ complexes and other *o*-hydroxyarylcarbonyl compounds^(2–6). Interestingly the intensity of this band is found to increase with the atomic number of lanthanone; this can be correlated with the dipole moment of the metal-oxygen bond, which is known to increase correspondingly⁽⁵⁾.

The bands at 1270, 1290 and 1240 cm^{-1} are assigned to the phenolic C–O stretching mode⁽¹¹⁾ of the three ligand

Table 1. Analyses and magnetic moments.

X	Complex	Found (Calcd.) %			μ_{eff} B.M.
		M	C	H	
H	YL ₃	11.7(11.73)	–	–	0
	LaL ₃	17.7(17.19)	67.3(66.83)	4.3(4.11)	0
	NdL ₃	17.6(17.74)	66.9(66.40)	4.2(4.09)	3.7
	GdL ₃	18.9(19.01)	–	–	8.3
	DyL ₃	19.5(19.54)	–	–	10.6
Me	YL ₃	11.1(11.12)	–	5.0(4.62)	0
	LaL ₃	16.1(16.34)	68.4(67.76)	5.0(4.59)	0
	NdL ₃	16.8(16.87)	68.2(67.34)	–	3.7
	GdL ₃	17.9(18.09)	–	–	7.9
	DyL ₃	18.1(18.61)	–	–	10.6
Cl	YL ₃	10.4(10.32)	–	3.9(3.31)	0
	LaL ₃	15.2(15.24)	60.4(59.26)	4.0(3.30)	0
	NdL ₃	15.7(15.74)	61.2(58.92)	–	3.6
	GdL ₃	16.6(16.90)	–	–	8.3
	DyL ₃	16.7(17.38)	–	–	10.5

molecules. These shift to lower frequencies in the spectra of the chelated complexes. Likewise, carbonyl stretching frequencies in the ligands appearing at 1642 cm^{-1} (1), 1640 cm^{-1} (2) and 1650 cm^{-1} (3) shift to $\sim 1600 \text{ cm}^{-1}$ in all the complexes. This indicates that the carbonyl oxygen is involved in the coordination with the metal ion. It may be noted that the $\nu(\text{C}=\text{C})$ (external) and $\nu(\text{C}-\text{C}-\text{Ph})$ in plane (adjacent to ring 2) increase in frequency (by 20 and 40 cm^{-1} , respectively) in the complexes as compared to their values in the corresponding free ligands (marked H in the Table). We account for such upward shifts as follows. Although there is conjugation

Table 2. Infrared spectral bands in cm^{-1} .

X	M	$\nu(\text{C}=\text{O})$	$\nu(\text{Ph}-\text{CH}=\text{CH}-)$	$\nu(\text{Ph}-\text{C}-\text{C})$ in plane	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$
H	H	1642	1565	1485	1270	–
	Y	1608	1588	1528	1255	478
	La	1605	1590	1530	1255	470
	Nd	1605	1588	1538	1260	470
	Gd	1607	1585	1525	1253	472
	Dy	1608	1586	1528	1255	488
Me	H	1640	1570	1686	1290	–
	Y	1625	1590	1523	1260	485
	La	1620	1590	1525	1260	490
	Nd	1615	1583	1521	1255	480
	Gd	1620	1585	1525	1258	485
	Dy	1618	1585	1520	1258	490
Cl	H	1650	1580	1478	1240	–
	Y	1604	1590	1520	1193	484
	La	1600	1590	1530	1195	480
	Nd	1600	1588	1525	1192	488
	Gd	1603	1588	1530	1200	470
	Dy	1600	1580	1510	1195	480

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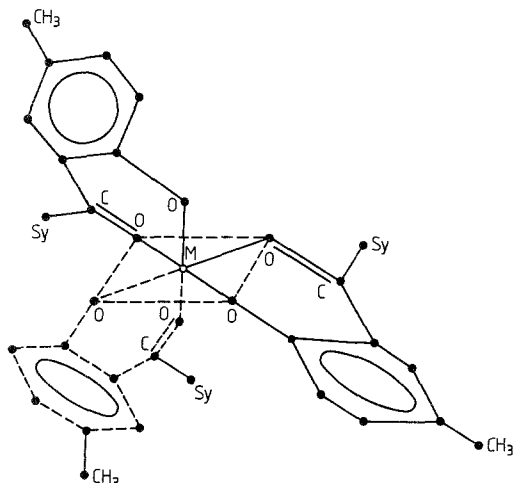


Diagram 2. Perspective drawing of rare earth chelates, showing the central metal ion coordinated to the three ligands (Sy = CH=CHPh).

between the external double bond and the carbonyl group, the conjugative interaction of the phenyl ring (1) with the carbonyl is greater because of the extra stability arising from the chelation. Consequently, the drift of electron density from ring (1) towards the metal centre will be more pronounced and this can also take place in the direction of the external double bond, thus accounting for an upward shift of stretching force constants.

The visible spectra of the neodymium complexes show pronounced absorptions in the regions *ca.* 17 200, *ca.* 13 330, and *ca.* 12 370 cm⁻¹ assigned to transitions to the states ⁴G_{5/2}, ⁴F_{7/2}

and ⁴F_{5/2}, respectively. On this basis, a tris-chelated symmetrical structure of the ligands around the central metal ion is proposed.

Experimental

The ligands were synthesised by known general procedures⁽¹²⁾. The complexes were prepared by mixing an ethanolic solution of the ligand with an ethanolic solution of the metal chloride (3 : 1) and raising the pH to *ca.* 6 with dilute alcoholic ammonia. The i.r. spectra were recorded in a Perkin Elmer 577 (KBr disc) and the electronic spectra in a Perkin Elmer 402 (in DMF). Magnetic measurements were made at room temperature by the Gouy technique.

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E.p.r. Studies of the Effect of Extensive Conjugation of Coordinated C=O and C=N in some Copper(II) Complexes

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Summary

E.p.r. studies indicate the delocalisation of the unpaired electron in the Cu^{II} complex of 2'-hydroxychalcone into the benzene ring. The 2-hydroxycrotonophenone complex has decreased covalency in the M–O σ -bond. The e.p.r. parameters of these complexes in pyridine solution show that their adducts are formed. A good correlation of magnetic properties with bonding characteristics has been obtained. The σ -bond covalency parameter shows a linear relationship with N_{iso} values which follow the order: ethylenediamine > N–Me > N-alkyl > N–H in the chalconeimine complexes.

Introduction

Infrared and optical spectral studies on metal(II) 2-hydroxycrotonophenone complexes reveal that conjugation of C=O with C=C enhances the ligand field strength⁽¹⁾. Further extension of conjugation, as in the 2'-hydroxychalcone complex (1), facilitates extensive $d\pi-\pi_3^*$ interaction leading to a low-spin square-planar configuration⁽²⁾. However, the corresponding chalconeimine⁽³⁾ and chalconeoxime⁽⁴⁾ complexes are high-spin octahedral or tetrahedral species. In order to amplify these observations, e.p.r. studies directly having a bearing on the electronic structures of complexes were undertaken. In the present work copper(II) complexes of crotonophenone, chalcone and chalconeimine and oxime have been investigated in frozen solutions and, in some cases, in polycrystalline copper(II) doped metal complexes. Attempts have been made to

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