Metal Complexes of 1,1,1,7,7,7 -Hexafluoroheptane-2,4,6-trione

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The preparation and properties of magnesium, cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 1,1,1,7,7,7-hexafluoroheptane-2,4,6-trione are reported. The ligand is capable of aiding coordinative saturation of the metal atoms in the binuclear complexes formed.

Introduction

Divalent binuclear chelates of heptane-2,4,6-trione have been studied extensively, and the structural and magnetic properties of these, and related compounds, have recently been reviewed [1]. The chemical behaviour of these metal triketonates is expected to parallel that of corresponding metal β-diketonates, and so it is anticipated that their fluorinated analogues would exhibit the ability to induce coordinative saturation of the metal. As part of our investigations in this area [2] we have synthesised divalent binuclear chelates of 1,1,1,7,7,7-hexafluoroheptane-2,4,6-trione (H_2hfda).

Experimental

Ethyltrifluoroacetate (12 g), acetone (1.74 g) and sodium hydride (50% dispersion: 7.2 g) were reacted together following the method of Miles *et al.* [3]. After addition of concentrated HCl, and extraction with ether, removal of the solvent yielded a clear viscous oil which was used without further purification [4]. The m.s. gave a molecular ion at m/e 250 amu, which corresponds to the calculated m.w. for $C_7H_4F_6O_3$. The i.r. gave bands at 1670, 1640, 1260–1060(bd), 1020, 950 and 845 cm^{-1}.

Metal Complexes

1,1,1,7,7,7-hexafluoroheptane-2,4,6-trione was added in stoichieometric amount to the metal(II) acetate dissolved in water and stirred vigorously. For copper and nickel precipitates were immediately formed, but for magnesium, cobalt and zinc, dilute ammonia solution was added to facilitate precipitation. The precipitates were collected and dried in a vacuum dessicator.

The i.r. spectra were recorded as KBr discs using a Perkin Elmer 457 Spectrometer and the major peaks are as follows:

Mg_2(hfda)$_2$·4H$_2$O. : 3400, 1640, 1555, 1505, 1490, 1275, 1210, 1190, 1120, 995, 890, 720, 629, 578, 510, 435 and 360 cm^{-1}.

Co_2(hfda)$_2$·4H$_2$O : 3400, 1625, 1550, 1500, 1470, 1270, 1205, 1185, 1140, 992, 888, 720, 630, 588, 510, 430 and 365 cm^{-1}.

Ni_2(hfda)$_2$·4H$_2$O: 3400, 1625, 1550, 1490, 1475, 1275, 1210, 1185, 1140, 998, 892, 725, 650, 595, 515, 440 and 370 cm^{-1}.

Cu_2(hfda)$_2$·2H$_2$O: 3420, 1620, 1550, 1490, 1278, 1218, 1190, 1140, 1000, 895, 730, 670, 650, 600, 510, 440 and 370 cm^{-1}.

Zn_2(hfda)$_2$·2H$_2$O : 3400, 1630, 1555, 1500, 1475, 1275, 1210, 1190, 1140, 990, 890, 725, 629, 588, 510, 420 and 365 cm^{-1}.

Results and Discussion

H_2hfda was prepared by the reaction of acetone, ethyltrifluoroacetate and sodium hydride in 1,2-dimethoxyethane, using the method of Miles *et al.* [3]. The product was a viscous oil which was not further purified [4] but treated directly with metal(II) acetates in aqueous solution to yield the corresponding divalent metal complexes, M_2(hfda)$_2$·nH$_2$O, (I), as precipitates (see Table). The reaction was immediate for copper and nickel but for the other metals, (magnesium, cobalt, and zinc), dilute ammonia solution was added to effect the precipitation.

(I)
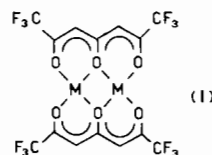
The infrared spectra of the metal complexes showed characteristic bands in the 3000–3400 cm^{-1} and 1500–1700 cm^{-1} areas. The broad band at 3200–3400 cm^{-1} may be assigned to coordinated water and has also been observed in the non-fluorinated complexes M_2(daa)$_2$·4H$_2$O [M = Co, Ni; daa = heptane-2,4,6-trione] [5]. The bands observed around 1650 cm^{-1} may be attributed to the coordinated C–O stretching modes and the absence of

TABLE. Analytical Data.

Compound	Colour	Found		Calculated	
		% C	% H	% C	% H
Mg₂(hfda)₂·4H₂O	Off—white	27.9	2.2	27.3	1.0
Co₂(hfda)₂·4H₂O	Red—Brown	24.5	2.1	24.5	1.8
Ni₂(hfda)₂·4H₂O	Green	24.6	2.1	24.5	1.8
Cu₂(hfda)₂·2H₂O	Yellow—Green	26.3	1.7	26.2	1.3
Zn₂(hfda)₂·2H₂O	Off-white	25.1	1.8	25.4	1.2

further bands at higher frequency due to noncoordinated carbonyl groups is indicative of total carbonyl group involvement in metal coordination [5]. There is a distinct shift from the frequency observed for ν_{CO} in the free ligand, 1680 cm^{-1}. It is probable that the latter exists primarily in the bis-enol form. The frequency shift observed on complexation is greater for copper than for magnesium. This is in keeping with the concept that the Mg—O bond would be weaker, or more ionic in character, than the Cu—O (or transition metal—oxygen) bond, and parallels the trend exhibited in the corresponding metal(II) hexafluoroacetylacetonates, [M(hfac)₂·nH₂O] [6].

Five metal-sensitive bands were observed in the region 720—350 cm^{-1}. These were assigned as metal—oxygen stretching bands, albeit containing varying degrees of M—O character, on the basis of the metal ion substitution method of Thornton *et al.* [7]. The M—O stretching frequencies were found to follow the Irving—Williams stability order, cobalt(II) < nickel-(II) < copper(II) > zinc(II). For M(hfac)₂, the band at 427 cm^{-1} in the spectrum of Cu(hfac)₂·H₂O has been assigned as the Cu—O stretching frequency [8] those at 404 and 385 cm^{-1} respectively in the spectra of Ni(hfac)₂ and Zn(hfac)₂ have been assigned to the Ni—O and Zn—O stretching frequencies [8].

The diffuse reflectance spectra of the tetra-hydrated metal complexes show two bands at 11,100 and 16,500 cm^{-1} for the nickel(II) chelate and at 9,000 and 17,500 cm^{-1} for the cobalt(II) chelate. These correspond with the values observed for the non-fluorinated analogues [5] and suggest that the coordination structure around the central metal atoms is octahedral. The dihydrated copper complex shows a band at 12,500 cm^{-1}. This may be compared with the values observed for Cu₂(daa)₂, 14,700 cm^{-1}, and for Cu₂(daa)₂(pyridine)₂, 13,520 cm^{-1} [5]. The former is described as square planar, and the latter complex has been shown, by X-ray structure determination [9], to contain two square pyramidal copper atoms. The triketonate ligands are terdentate and planar. Each copper atom is bound to four coplanar O atoms (with the central O atoms of the ligands linking the copper atoms) and to one pyridine N atom. The pyridine ligands are on opposite sides of the molecule (A).

The dicopper complex of ditrifluoroacetylcyclopentanone has been reported as a dihydrate [1]. The X-ray structure shows that the two water ligands are on the same side of the molecule, leaving the vacant apical sites on copper available for weak interaction with the oxygen atoms of a second dicopper complex. This gives a dimeric, tetranuclear species with copper(II) achieving six coordination.

The d.r.s. band at 12,500 cm^{-1} corresponds to the bands observed in six-coordinated Cu(hfac)₂ derivatives [10], but in the absence of structural data it is not possible to assign which of the two forms, A or B, is taken up by Cu₂(hfda)₂·2H₂O; or if both waters are coordinated to one copper.

The mass spectra of the transition metal complexes were recorded and show as the molecular ion anhydrous M₂(hfda)₂. This parallels the behaviour observed for M(hfac)₂·nH₂O where M(hfac)₂ is observed as the molecular ion [8]. There are many metal-containing fragments in the spectra, arising principally from loss of —F and —CF₃ from the ligands. The species M(hfda) was found in all cases and is the consequence of symmetrical cleavage of the molecular ion. The product of asymmetric cleavage, M₂hfda, was observed only for copper, and may reflect the stability of the lower formal oxidation state of copper. In contrast with Cu₂(daa)₂, no species of the type Cu(daa)₂ were detected [9].

The magnetic moment at room temperature of Cu₂(hfda)₂·2H₂O was determined and found to be 1.33 B.M. (per copper(II) ion). It is possible to view this value which, although reduced from the spin only value, is somewhat higher than those for comparable non-fluorinated copper(II) triketonates [1], as a reflection of the high electron withdrawing power of the —CF₃ groups. These could in effect, remove electron density from the Cu₂O₆ unit and so inhibit any superexchange mechanisms.

The reaction of Cu₂(hfda)₂·2H₂O with coordinating ligands has been the subject of a preliminary investigation. The reaction with pyridine leads to the

isolation of $Cu_2(hfda)_2 \cdot 2pyr \cdot 2H_2O$ if the reaction is carried out either in toluene solution, or by slow aerial evaporation of a saturated pyridine solution of the precursors. Bipyridyl and *o*-phenanthroline give complexes of the type $Cu_2(hfda)_2L_2$ and also Cu_2-$(hfda)_2L \cdot 4H_2O$. The anhydrous bipyridyl complex however contained a benzene of solvation. The reaction with ethylenediamine gave a wide range of products of varying stoichieometry. It would be premature to postulate the precise nature of these complexes in the absence of structural determinations. It would appear though that coordinative saturation of copper(II) is achieved.

Acknowledgement

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