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Metal Complexes of 1,1,-[1,3-Phenylene]-bis-1,3-Butanedione

D. E. FENTON, C. M. REGAN

Department of Chemistry, The University, Sheffield, S3 7HF, UK

U. CASELLATO, P. A. VIGATO

Laboratorio di Chimica e Tecnologia dei Radioelementi CNR, Area della Ricerca, Corso Stati Uniti, 35100 Padua, Italy

and M. VIDALI

Istituto di Chimica Generale, Università di Padova, Via Loredan, 4, 35100 Padua, Italy

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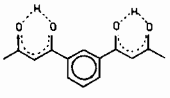
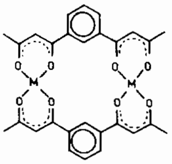
Transition metal complexes of β-diketones and β-triketones are well documented in the literature [1, 2]. Information concerning similar complexes of tetraketones is restricted to an account of the synthesis of the copper(II), cobalt(II) and nickel(II) complexes of 1,7-diphenyl-1,3,5,7-heptanetetraone [3]. As part of our joint programme concerning the design and synthesis of ligands capable of homo- and heterobinuclear complexation we have synthesised the tetraketone 1,1′-[1,3-phenylene]-bis-1,3-butanedione, (I), and investigated its properties.

The ligand is prepared by an adaptation of the method of Wittig [4]. This involved the condensation of the requisite diacetylbenzene with ethylacetate in the presence of sodium wire, and the ligand was recovered in good yield. (I) was characterised by i.r., m.s. (P^+ at m/e = 246) and nmr spectral data. ^1H nmr ($CDCl_3$): 2.22(6H,s,CH_3), 6.23(2H,s,CH), 7.53, 8.03, 8.35(4H, multiplets, aromatic ring) and 10.70 ppm(2H,s,OH); ^{13}C nmr ($CDCl_3$): 25.78(CH_3), 96.88(CH), 125.40, 128.92, 130.37, 135.29 (aromatic ring), 182.18 and 194.08 ppm(C–OH, enol forms). The ligand exists in virtually 100% enol form in $CDCl_3$.

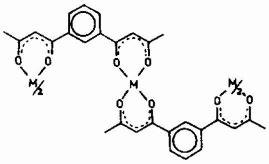


The reaction of metal acetate in hot ethanol with (I) in the same solvent led to the precipitation of $Cu_2(I)_2$; $Ni_2(I)_2\cdot 4H_2O$; $Mn_2(I)_2\cdot 4H_2O$; $Zn_2(I)_2$ and $Mg_2(I)_2\cdot 3H_2O$. The cobalt complex, $Co_2(I)_2\cdot 4CH_3OH$, was prepared, under dinitrogen, from reaction of cobalt(II) acetate with (I) in degassed CH_3OH. The iron complex, $Fe_2(I)_2\cdot{}_2H_2O$ was prepared from ferrous sulfate and (I) under similar conditions. The complexes are relatively insoluble in the common organic solvents but soluble in coordinating solvents such as pyridine. Purification was effected using Soxhlet extraction procedures to remove excess ligand, or metal acetate. The reaction of oxovanadium(IV) acetate with (I) in ethanol gave two products $(VO)_2(I)_2\cdot H_2O$ and $VO(I)_2\cdot H_2O$. No other mononuclear complexes have yet been isolated.

Two structural forms, (A) and (B), may be proposed for the binuclar complexes.



(A)



(B)

The availability of P^+ corresponding to the monomer (A) in the m.s. of the Cu_2, Ni_2 and Zn_2 complexes, together with the absence of higher peaks leads to the proposal that (A) is the form adopted. The i.r. of the complexes are similar in pattern throughout the series. The magnetic moment for the Cu_2 complex is that for an isolated Cu atom, an no antiferromagnetic coupling is detected.

The isolation of $Cu_2(I)_2$ compared with the solvated nickel and cobalt complexes parallels the behaviour of the corresponding triketones [2]. Axial ligation to effect coordinative saturation can occur at either or both metal atoms as has been seen in the series of complexes isolated. The reaction of the copper and nickel complexes with pyridine leads to the isolation of $Ni_2(I)_2\cdot 4$pyr but the copper complex readily loses pyridine on exposure to the atmosphere.

Complexes of uranyl(VI) and thorium(IV) have been synthesised by the reaction of (I) in MeOH–H_2O with LiOH and the corresponding metal nitrate. The uranyl complex is binuclear and solvated, $(UO_2)_2(I)_2\cdot 2H_2O$, and is soluble in MeOH and pyridine. This would suggest a non-polymeric structure as in (A). The coordination about each uranium atom is a pentagonal bipyramid as in UO_2(β-dike)(H_2O) [5]. The two water molecules can be replaced by neutral monodentate ligands (L) giving $(UO_2)_2(I)_2(L)_2$.

The stoichiometry of Th(IV) complex is $Th(I)_2$. By comparison with Th(β-diketonate)$_4$ the metal is either square antiprismatic (D_2) or dodecahedral (D_{2d}) [5]. Consequently we suggest that the complex may be either binuclear, $Th_2(I)_4$, or polynuclear in a manner similar to (B). $Th(I)_2$ is considerably less soluble in organic solvents than the uranyl(VI) complex $(UO_2)_2(I)_2 \cdot 2H_2O$.

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