Eight-co-ordinate Complexes containing a Single *d*-Electron

By R. L. DEUTSCHER, and D. L. KEPERT*
(*The University of Western Australia, Nedlands, Western Australia*)

ATTEMPTS to describe the crystal-field splitting of *d*-orbitals in an eight-co-ordinate crystal field are not in good agreement with each other,[1] and have not been experimentally confirmed. As a continuation of our earlier work[2] on the preparation of eight-co-ordinate complexes containing a single *d*-electron, we report the first β-diketone, tropolone, and 8-hydroxyquinoline complexes of this type.

Niobium tetrachloride reacts with benzoyltrifluoroacetone (btaH), thenoyltrifluoroacetone (ttaH), and dibenzoylmethane (bzbzH) in anhydrous toluene or acetonitrile in the presence of bases such as triethylamine, to yield tetrabis-β-diketonatoniobium(IV). Tropolone (tH) and 8-hydroxyquinoline (oxH) similarly form $Nb^{IV}t_4$ and $Nb^{IV}ox_4$ respectively. The corresponding acetylacetone complex was prepared from $NbCl_4$ and Tl acac. In all cases the i.r. spectra indicate that the ligands are bidentate and equivalent.

The acetylacetone complex is too air-sensitive for microanalysis, but forms the more stable adduct Nb acac$_4$,dioxan.

The effective magnetic moment of the acetylacetone complex (1·51 B.M.) is significantly lower than for the other eight co-ordinate complexes (1·60—1·66 B.M.). The nine-co-ordinate Nb acac$_4$,dioxan has the spin-only value of 1·73 B.M. These values may be compared with moments of approximately 1·3 B.M. for complexes of octahedral niobium(IV).[3]

These complexes show the expected absorption bands in the u.v. spectrum above 25,000 cm.$^{-1}$, due to electronic transitions within the ligand, which are also present in the corresponding zirconium complexes. In addition the niobium complexes show two bands in the visible region which although of high ε (3000—5000), are assigned to *d–d* transitions (Table). All other bands in the region

Spectra (<25,000 *cm.*$^{-1}$) *of* d^1 *eight-co-ordinate complexes*

Complex	Diffuse reflectance (cm.$^{-1}$)		Solution (cm.$^{-1}$)	
Nb acac$_4$	7000	15,500		
Nb bzta$_4$	13,000	21,000	14,000	21,700
Nb tta$_4$	13,000	20,500	13,700	20,800
Nb bz[illegible]$_4$	10,000	20,000	12,500	21,000
Nb c[illegible]	12,000	17,500	12,400	19,200
N[illegible]ac$_4$,dioxan	9000	15,000		

25,000—500 cm.$^{-1}$ can be assigned to ligand vibrations. The different behaviour of acetylacetone compared with the other β-diketones is also shown by the lower energy of these *d–d* bands. This is in marked contrast to complexes between these α-diketones and other metals, where acetylacetone produces the largest crystal field splitting. This suggests that the acetylacetone complex has a different stereochemistry to the other complexes, in agreement with the known dodecahedral stereochemistry of M bzbz$_4$ (M=Ce, Th, and U)[4] and (Pr tta$_4$)$^-$,[5] the square antiprismatic stereochemistry of M acac$_4$ (M=Ce, Zr, Hf, Th, and U),[6] and with our previous conclusion that the more polarisable ligands tend to form dodecahedral complexes.[7] The visible spectra can therefore be used to predict that the other β-diketone complexes are dodecahedral.

The two *d–d* bands are shifted significantly in solution (Table), but are independent ($\pm$200 cm.$^{-1}$) of the solvent used (acetone, toluene, dioxan), showing that the stereochemistry becomes significantly distorted in the solid state. Previous calculations have shown that it is relatively easy to distort eight co-ordinate polyhedra.[8,9]

If the spectrum of Nb acac$_4$ is compared with a crystal field splitting diagram for a square antiprism calculated as a function of θ, the angle the metal–ligand bond makes with the eight-fold inversion axis, it can be deduced that $\theta \sim 55°$, which is in reasonable agreement with previous calculations and with other square antiprismatic molecules.[8] A similar procedure for the other tetrakis-β-diketonatoniobium complexes does not lead to a unique set of values for θ_A and θ_B, the parameters which define a dodecahedron; for example if $\theta_A = 40°$, then $\theta_B \sim 74°$, or if $\theta_A = 36°$, then $\theta_B \sim 78°$. These are again in reasonable agreement with the expected values.[8] The spectral differences between solid and solution can be accommodated by changing the angular parameters by only *ca.* 2°.

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