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Crystal Structure of a Nickel(II) Complex, $NiBr_2(C_5H_8O_2)_2$, containing Ketonic Molecules of Acetylacetone

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Summary A molecular complex $NiBr_2(C_5H_8O_2)_2$ in which ketonic acetylacetone molecules act as bidentate ligands has been synthesised and its crystal structure shown to contain chelate rings of boat conformation.

In a previous communication a molecular complex of $MnBr_2$ and acetylacetone, $MnBr_2(C_5H_8O_2)_2$ was reported to involve enolic molecules of acetylacetone as unidentate ligands.[1] The corresponding nickel(II) complex has been found to contain ketonic molecules of acetylacetone as bidentate ligands.

When bis(acetylacetonato)nickel(II) was allowed to react with twice as many mols of dry hydrogen bromide in dichloromethane containing a large excess of acetylacetone, a light green precipitate was obtained which analysed as $NiBr_2(C_5H_8O_2)_2$. No suitable solvent was available, but the absorption spectrum of a solid specimen in Nujol mull exhibits maxima at 695 and 405 nm, which, together with the magnetic moment of 3·39 B.M., indicate an octahedral structure. An i.r. spectrum shows a very strong carbonyl stretching absorption at 1693 cm^{-1} suggesting the co-ordination of ketonic acetylacetone molecules.[2] This is in contrast to the spectrum of $MnBr_2(C_5H_8O_2)_2$[1] [ν(CO) 1627 cm^{-1}], but resemblance to the spectra of $CoBr_2(C_5H_8O_2)_2$[3] and $[Ni(C_5H_8O_2)_3](ClO_4)_2$[4] which have already been reported. In order to confirm the mode of linkage, a single crystal *X*-ray analysis of the present complex was performed.

Green prismatic crystals suitable for *X*-ray work were obtained by the recrystallization of the compound from a 1:1 mixture of nitromethane and acetylacetone. Since they are hygroscopic, the specimens were sealed in thin-walled glass capillaries. *Crystal data:* monoclinic, $a = 7·72$, $b = 12·64$, $c = 7·34$ Å, $\beta = 103·6°$, $Z = 2$, $D_c = 2·0$ g cm^{-3}, space group $P2_1/n$. Intensities of 679 independent reflections were visually estimated from multiple-film equi-inclination Weissenberg photographs taken around the *a* axis with Ni-K_α radiation. The structure was solved by the conventional Patterson and Fourier methods. The positional and isotropic thermal parameters were refined by the least-squares method to an *R* factor of 0·12.

The perspective drawing of the complex molecule is shown in the Figure. The nickel atom occupies a centre of symmetry and has a tetragonally distorted octahedral co-ordination by the four oxygen and two bromine atoms. The acetylacetone molecule in $MnBr_2(C_5H_8O_2)_2$[1] is unidentate and planar, but in the present complex the acetyl-

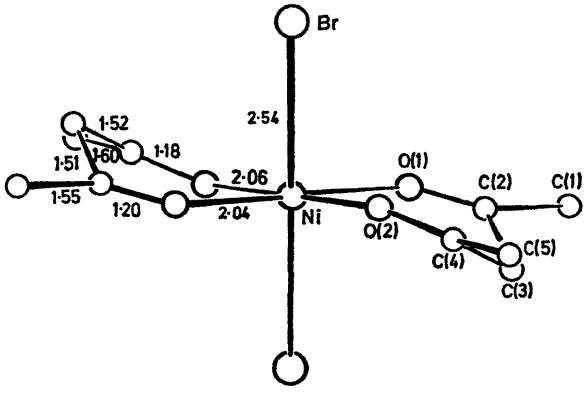

Figure. trans-*Dibromobis(acetylacetone)nickel*(II) *with the bond lengths* (Å). *The e.s.d.s on the bond lengths between light atoms are* 0·04 Å. *Bond angles are:* O(1)–Ni–O(2) = 86·7(4)°, C(2)–C(3)–C(4) = 114(2)°.

acetone molecule is bidentate and its two planar acetone moieties are at a dihedral angle of 151°. The chelate ring takes a boat conformation which has an approximate mirror plane bisecting the angle O(1)–Ni–O(2). The dihedral angle between the plane Ni–O(1)–O(2) and the plane O(1)–O(2)–C(4)–C(2) is 19°, and that between the latter and the plane C(2)–C(3)–C(4) is 29°. These structural features confirm the presence of ketonic acetylacetone molecules.

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[1] S. Koda, S. Ooi, H. Kuroya, Y. Nakamura, and S. Kawaguchi, *Chem. Comm.*, 1971, 280.
[2] R. Mecke and E. Funck, *Z. Elektrochem.*, 1956, **60**, 1124.
[3] Y. Nakamura and S. Kawaguchi, *Chem. Comm.*, 1968, 716.
[4] P. W. N. M. van Leeuwen, *Rec. Trav. chim.*, 1968, **87**, 396.