The Structure of the Cobalt(II) Derivative of the Sulphur Chelate, Dithioacetylacetone

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RECENTLY Martin and Stewart[1] have reported the successful syntheses of a number of transition-metal derivatives of the previously unknown ligand, dithioacetylacetone. For these compounds the ligand is prepared *in situ* and has never been isolated. The evidence reported on the structure of the cobalt(II) compound suggested that the metal environment is square planar. This and the molecular structure of the ligand have been confirmed by a single-crystal structure determination, using X-ray diffraction techniques. Further studies have shown that the nickel(II) derivative is isostructural with the cobalt(II) compound.

The crystal data for bis(dithioacetylacetonato)-cobalt(II) are as follows: $C_{10}H_7S_2Co$, $M = 218$, orthorhombic, $a = 15{\cdot}64$, $b = 14{\cdot}35$, $c = 6{\cdot}05$ Å, $U = 1357$ Å, $Z = 4$, space group $Cmca$ (D_{2h}^{18}, No. 64), Cobalt unfiltered radiation, single-crystal oscillation and Weissenberg photographs.

From symmetry considerations the cobalt atoms were assigned to the special positions of the type $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + (0, 0, 0; 0, \frac{1}{2}, \frac{1}{2})$ which are sites of symmetry $2/m$. A three-dimensional Patterson function calculated using 437 terms revealed the positions of the sulphur atoms. All of the other atoms (excepting the hydrogen atoms) were located in a subsequent three-dimensional electron density distribution. The structure is being refined using the method of least squares, applying individual anisotropic temperature factors; at present the R factor is 0·13.

Crystals of bis(dithioacetylacetonato)cobalt(II) are composed of discrete monomeric molecular units which are almost perfectly planar. Each molecule is separated from its neighbours at the normal van der Waals distances. The metal atom of each unit is surrounded by four sulphur atoms and all five atoms are exactly coplanar, a restriction imposed by the crystal symmetry. The molecular geometry and dimensions are given in the Figure.

The stereochemistry of cobalt(II) is normally such that it displays an octahedral or a tetrahedral configuration in its complexes. It seems that the square-planar environment found for the cobalt atom in bis(dithioacetylacetonato)cobalt(II) is rare, for in only three compounds has this stereochemical form for cobalt(II) been reported. These compounds are di(tetra-n-butylammonium)bis(maleonitriledithiolate)cobalt(II),[2] *trans*-dimesitylbis(diethylphenylphosphine)cobalt(II),[3] and cobalt(II) phthalocyanine.[4]

The short cobalt–sulphur distance of 2·16 Å (with an estimated standard deviation of 0·008 Å) found in bis(dithioacetylacetonato)cobalt(II) is exactly that reported for the cobalt–sulphur distance in di(tetra-n-butylammonium)bis(maleonitriledithiolate)cobalt(II).[2] The carbon–sulphur bond distances of 1·70 Å (with an estimated standard deviation of 0·015 Å) and the carbon–carbon bond lengths within the chelate rings of 1·38 Å (with an estimated standard deviation of 0·02 Å) are comparable with values one would expect in a system where extensive delocalization would be predicted. We must state that as refinement is incomplete the bond lengths quoted for our compound are only provisional.

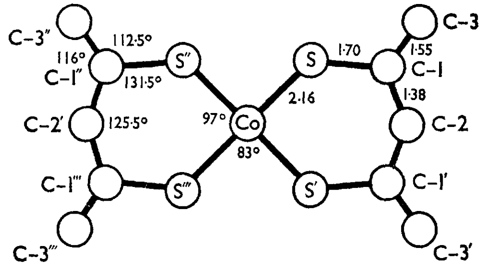

FIGURE. *Atomic disposition and molecular dimensions bis(dithioacetylacetonato)cobalt*(II).

Single-crystal *X*-ray photographs of the nickel derivative of dithioacetylacetone showed that it crystallizes in the same space group and with almost the same cell dimensions as the cobalt(II) compound: $a = 15{\cdot}9$, $b = 14{\cdot}4$, $c = 6{\cdot}18$ Å. Since the intensity data distributions for the two compounds were almost identical it was concluded that the two sets are isostructural.

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