Lattice Compounds of *NN'*-Ethylenebis(acetylacetoneiminato)-complexes with Amine Perchlorates

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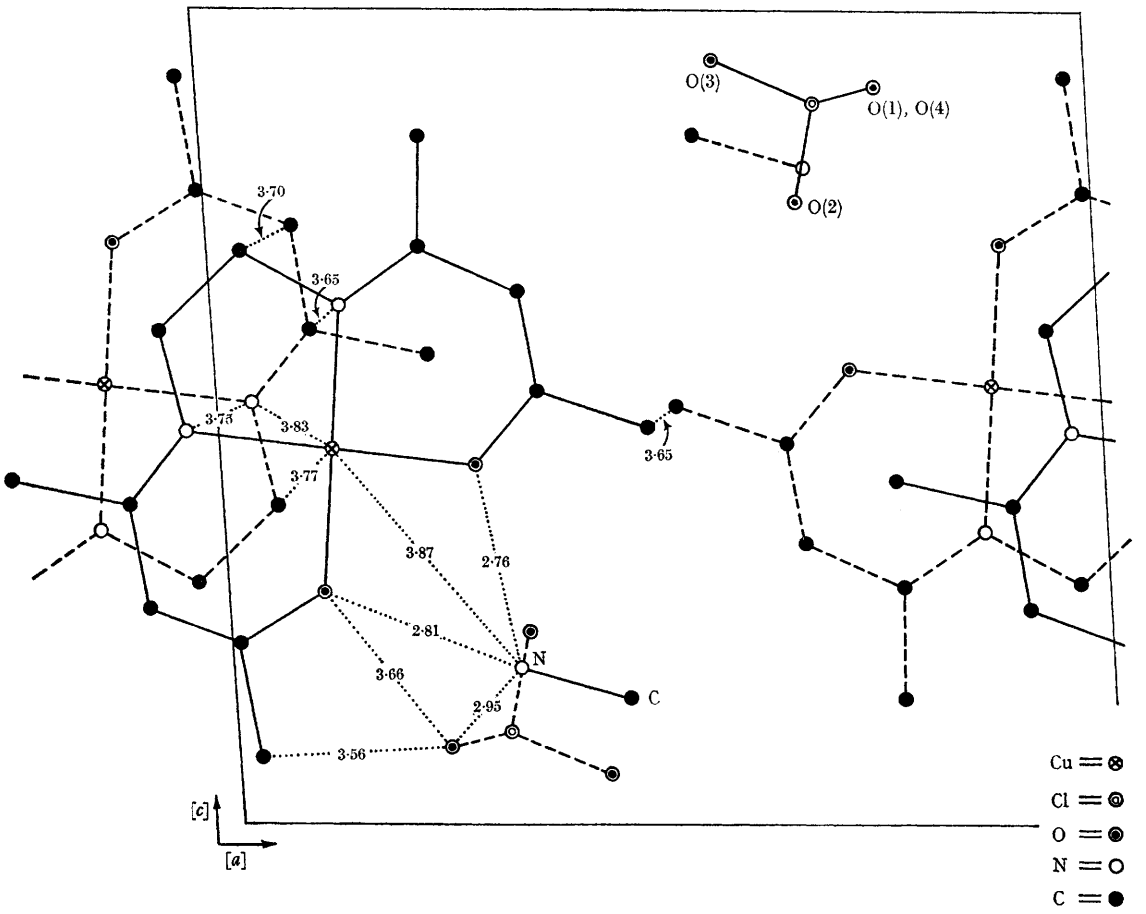
DURING the course of an investigation into reactions of metal–amine complexes with carbonyl compounds it was observed that ethylenediamine-nickel perchlorates reacted with acetylacetone in methanol and acetonitrile solutions to yield a diamagnetic brown crystalline product of analytical composition $C_{13}H_{23}N_3NiO_2(ClO_4)$. The infrared spectrum of this material indicated the presence of C:N and/or C:C groups, as well as $R–NH_3^+$ groups. Solutions in methanol had the properties expected of a mixture of *NN'*-ethylenebis-(acetylacetoneiminato)nickel(II) plus ethylenediammonium perchlorate in a 2 : 1 mole ratio, and the same product crystallised from solutions containing these constituents. A series of analogous compounds of the general formula $[M(en)–(acac)_2]$ $[R_nNH_{4-n}]$ ClO_4 were prepared (where M = Cu^{II} or Ni^{II}, and R_nNH_{4-n} represents a substituted, alicyclic, or aromatic amine) by crystallisation from alcoholic solutions of the constituents (using methanol or propan-2-ol depending upon the solubility of the product).

X-Ray powder patterns of the methylamine and ethylenediamine compounds indicate that in each case the copper and nickel analogues are isostructural. Studies of single crystals of $[CuC_{12}H_{18}N_2O_2]CH_3NO_3ClO_4$ show them to be monoclinic, $a = 11{\cdot}77$, $b = 7{\cdot}25$, $c = 10{\cdot}89$ Å, $\beta = 93{\cdot}5°$, 2 molecules per unit cell, space group $P2_1$ or $P2_1/m$. Three-dimensional intensity data were visually estimated from Weissenberg photographs, and the structure solved by conventional heavy-atom methods. The complex molecule, the methylammonium ion, and the perchlorate ion all exist independently, the former as *NN'*-ethylenebis(acetylacetoneiminato)copper(II). All non-hydrogen atoms other than two oxygens of the perchlorate ion lie in, or very near to, a plane perpendicular to (010). These two oxygens are reflection images across the plane, and the structure at least closely approximates the centrosymmetric space group. Refinement in $P2_1/m$ converged at $R = 0{\cdot}17$ when thermal parameters were assumed isotropic, and at $R = 0{\cdot}11$ when anisotropic. In the latter case some of the bond lengths and angles, and some of the thermal parameters, assumed unlikely values, and it was deduced that the structure really does show some distortion from $P2_1/m$ symmetry. The exact form of this distortion is currently being analysed, but the satisfactory agreement obtained between observed and calculated data demonstrates that the structure is substantially correct as presently described.

The structure is shown in the Figure, as are the



FIGURE

The structure as projected on to (010). *Atoms for which* y = 0 *are connected by full lines, atoms for which* y = ½ *by broken lines. Distances are in* Å.

close molecular approaches. It may be seen that while the methylammonium ion makes some approaches to oxygen atoms which may be hydrogen bonds, there is no other association, and the compound is a simple lattice complex. As the amine has no apparent function other than as a monovalent cation, attempts were made to co-crystallise the *NN'*-ethylenebis(acetylacetone-iminato)-complexes with sodium perchlorate, and the analgous compounds were indeed successfully prepared. It seems that the range of compounds which can be so obtained may only be restricted by solubility considerations.

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