

ω -Nitroacetophenone as a Chelating Agent: Its Complexes with Bivalent Metals of the First Transition Series

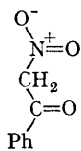
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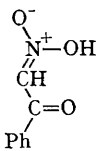
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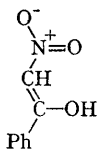
It is known¹ that ω -nitroacetophenone (I) (hereafter called ω -N.A.P.) can give rise, in solution in polar and nonpolar solvents, to tautomeric equilibria, which have been postulated to involve the isonitronic form (II) or the nitroenolic form (III), depending on the nature of the solvent.



(I)



(II)

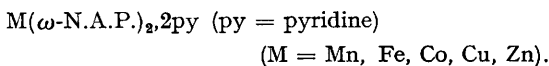
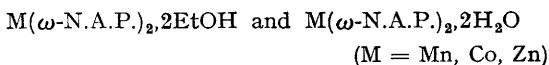
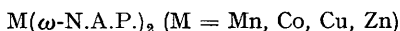


(III)

We have recently initiated an investigation of the ability of ω -N.A.P. to act as a chelating agent. The use of this compound was suggested (a) by the presence of an aliphatic nitro-group which, as far as we know, has never been used before in the formation of chelate complexes and (b) by the similarity of this chelating system with that of acetylacetone and of the β -diketones in general.

We have recently reported² some preliminary results of the synthesis and investigation of the structure of the complexes formed by ω -N.A.P.

with nickel(II). We have now prepared and studied a series of complexes with all bivalent metal ions of the first transition series from manganese to zinc. These complexes have the formulae:



Complexes of type $\text{M}(\omega\text{-N.A.P.})_2$ can easily be obtained by desolvation of the corresponding bis-ethanolates. $\text{Mn}(\omega\text{-N.A.P.})_2$ and $\text{Cu}(\omega\text{-N.A.P.})_2$ can also be prepared by treating ω -N.A.P. with the acetate of the metal in acetone. These two complexes are stable to air, $\text{Zn}(\omega\text{-N.A.P.})_2$ is slightly hygroscopic, whereas $\text{Co}(\omega\text{-N.A.P.})_2$, like $\text{Ni}(\omega\text{-N.A.P.})_2$, is rapidly transformed to the dihydrate. We give here some of the most significant results of the structural investigation carried out on some of these complexes.

The copper complex is the only one of this series of which we have been able to isolate single crystals

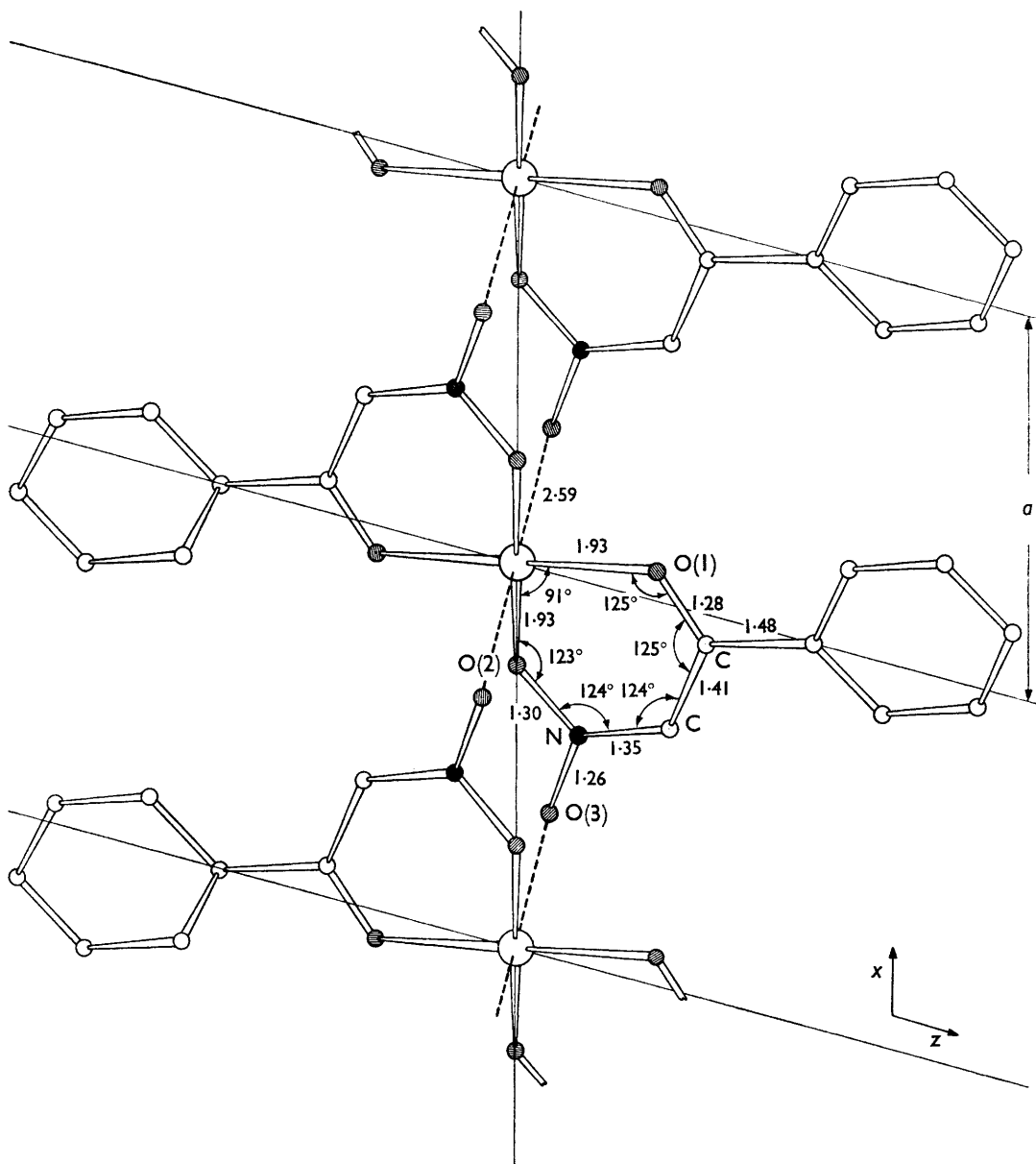


FIGURE. The polymeric system of complex molecules, projected along the b -axis on the x - z planes.

The average *e.s.d.*'s on the bond lengths are 0.004 \AA for Cu-O and 0.007 \AA for O-N, O-C, and C-C.

E.s.d. for the bond angle O(1)-Cu-O(2) is 0.2° ; for Cu-O(1)-C or Cu-O(2)-N 0.3° , and for the other cited angles 0.4° .

suitable for crystallographic work. This compound $(\text{C}_6\text{H}_5\text{NO}_3)_2\text{Cu}$, forms red-brown triclinic crystals, with cell dimensions $a = 5.453 \pm 0.01$, $b = 8.183 \pm 0.01$, $c = 9.506 \pm 0.01 \text{ \AA}$; $\alpha =$

$109^\circ 55' \pm 10'$, $\beta = 104^\circ 52' \pm 10'$, $\gamma = 90^\circ 21' \pm 10'$; $U = 383.4 \text{ \AA}^3$; $D_m = 1.71 \pm 0.02 \text{ g.cm.}^{-3}$ (by flotation); $Z = 1$; $D_c = 1.698 \text{ g.cm.}^{-3}$; $F(000) = 197.98$. Space group $\bar{P}1$ from morphology, and

structure determination. Data from Weissenberg photographs, Cu- K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$).

The X-ray intensities of 1259 independent reflections were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken about the a (6 layers) and the b axis (5 layers). From a three-dimensional Patterson synthesis the positions of all atoms were found, with the copper atom at the origin (centre). After preliminary Fourier refinement, co-ordinates and anisotropic temperature-factors were refined by least squares. Present values ($R = 8.4\%$) define the bond lengths (in \AA) and angles given in the Figure.

The centre of symmetry (at the copper atom) requires a *trans*-configuration for the molecule. The complex, including phenyl groups, is almost planar. The copper atom is surrounded by a distorted (elongated) octahedron of six oxygen atoms. By symmetry, the four oxygen atoms from the two ligands and the copper atom define a plane. The copper atom completes its co-ordination sphere with the oxygen atoms (not otherwise involved in the chelation) from neighbouring systems translated along the a axis. This repetition of Cu-O interaction produces a polymeric system (see Figure). Bond distances found indicate that in the metal-ligand system there is a considerable π -electron delocalization.

The reflectance spectrum (range 7000—23,000 cm^{-1}) carried out on solid $\text{Co}(\omega\text{-N.A.P.})_2$ indicates an octahedral structure for the compound. The spectrum of the complex in anhydrous benzene

shows the same structure in solution. Molecular-weight measurements carried out also in anhydrous benzene give evidence for the existence of a tetrameric molecule. This form of molecular association also shown by $\text{Ni}(\omega\text{-N.A.P.})_2$, which is trimeric in benzene solution, fulfils the octahedral co-ordination necessary to explain the spectroscopic behaviour both in solution and in the solid state.

Magnetic susceptibility measurements (77—300°K) both for $\text{Co}(\omega\text{-N.A.P.})_2$ and for the corresponding nickel complex, showed a strong temperature dependence for the magnetic moments, as expected for complexes with a strong antiferromagnetic interaction. However this result suggests that the type of molecular association in these two complexes differs from that found for $\text{Cu}(\omega\text{-N.A.P.})_2$ where, because of the distance between metal atoms, such interaction seems rather improbable. Structural models for these complexes are probably analogous to those known for the corresponding acetylacetonates.

Of the solvated complexes, those having formulae $\text{M}(\omega\text{-N.A.P.})_2 \cdot 2\text{X}$ ($\text{X} = \text{H}_2\text{O}$, pyridine) and $\text{Mn}(\omega\text{-N.A.P.})_2 \cdot 2\text{EtOH}$ are stable to air, whilst $\text{Co}(\omega\text{-N.A.P.})_2 \cdot 2\text{EtOH}$ and $\text{Zn}(\omega\text{-N.A.P.})_2 \cdot 2\text{EtOH}$ are transformed to the dihydrates, the Zn complex reaction being more rapid.

Magnetic susceptibility measurements, visible reflectance spectra, and crystallographic data permit assignment of distorted octahedral symmetry to all these complexes.

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¹ K. H. Meyer and P. Werthemer, *Ber.*, 1914, **47**, 2374.

² C. Ercolani, I. Collamati, and G. Sartori, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1963, **40**, 558.