

## Bis(biuretato)-complexes of Tervalent Copper, Nickel, and Cobalt

By J. J. BOUR and J. J. STEGGERDA

*(Department of Inorganic Chemistry, University of Nijmegen, Nijmegen, The Netherlands)*

THE complexes  $\text{Cu}^{\text{II}}\text{bi}_2^{2-}$ ,  $\text{Ni}^{\text{II}}\text{bi}_2^{2-}$ , and  $\text{Co}^{\text{III}}\text{bi}_3^{3-}$  in which  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ , and  $\text{Co}^{\text{III}}$  are co-ordinated to the dinegative ion of biuret ( $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 = \text{biH}_2$ ) are known.<sup>1,2</sup>

We report the synthesis of compounds of the type  $\text{KMbi}_2$  where  $\text{M} = \text{Cu}^{\text{III}}$ ,  $\text{Ni}^{\text{III}}$ , or  $\text{Co}^{\text{III}}$ . The  $\text{Cu}^{\text{III}}$  and  $\text{Ni}^{\text{III}}$  compounds can be prepared by the oxidation of  $\text{K}_2\text{Cubi}_2$  and  $\text{K}_2\text{Nibi}_2$  with  $\text{K}_2\text{S}_2\text{O}_8$  in 5N-KOH solutions at room temperature, the products being immediately precipitated. The composition of the products was analytically confirmed to be  $\text{KCubi}_2$  and  $\text{KNibi}_2$ . In the presence

of  $\text{Cu}^{\text{III}}$  and  $\text{Ni}^{\text{III}}$ , these compounds react with acidified potassium iodide solutions yielding 2 and 1 equiv. of  $\text{I}_2$  per mole  $\text{KCubi}_2$  and  $\text{KNibi}_2$ , respectively.

$\text{KCubi}_2$  (brown) and  $\text{KNibi}_2$  (blue-black) are insoluble in water and organic solvents, they do not react with atmospheric moisture and oxygen up to temperatures of about 250°. Reactions with aqueous hydrochloric and sulphuric acid at room temperature yield  $\text{Cl}_2$  and  $\text{O}_2$ , respectively.

Infrared spectra demonstrate the presence of biuretato-chelates as in the parent substances.

Magnetic susceptibilities of the solids were measured at 25° and found to be  $10 \times 10^{-6}$  for  $\text{KCubi}_2$  and  $2600 \times 10^{-6}$  c.g.s. per mole for  $\text{KNibi}_2$ , corresponding to effective magnetic moments of 0.4 and 2.5 B.M. The moment of the  $\text{Cu}^{\text{III}}$  complex is higher than can be expected for a low-spin  $d^8$  configuration, no explanation for this phenomenon can be given at this stage. The moment of the  $\text{Ni}^{\text{III}}$  complex is in the range (2.4—2.8 B.M.) found for the square-planar low-spin  $d^7$  configuration of  $\text{Co}^{\text{II}}$  complexes.

On heating an aqueous solution<sup>2</sup> of  $\text{Cobi}_3^{2-}$  for several hours while the pH was reduced to pH 8 by adding HCl,  $\text{KCobi}_2$  is precipitated as a yellow

product. X-Ray powder diagrams of  $\text{KNibi}_2$  and  $\text{KCobi}_2$  show them to be fully isomorphous.  $\text{KCubi}_2$  is however not strictly isomorphous but a closely related structure is suggested by its X-ray diagram. Further structural investigations are in progress. A comparison with the bis(biguanidino)silver(III) ion<sup>3</sup> should be interesting.

$\text{KCubi}_2$  is also formed when a suspension of  $\text{K}_2\text{Cubi}_2 \cdot 4\text{H}_2\text{O}$  in ethanol or benzene, containing HCl, is aerated at room temperature under u.v. irradiation. This reaction supports Anbar's hypothesis that  $\text{Cu}^{\text{III}}$  complexes are intermediates in copper-catalyzed oxidation reactions.<sup>4</sup>

(Received, December 1st, 1966; Com. 946.)

<sup>1</sup> H. C. Freeman, J. E. W. L. Smith, and J. C. Taylor, *Acta Cryst.*, 1961, **1**, 407.

<sup>2</sup> M. Kato, *Z. anorg. Chem.*, 1959, **300**, 84.

<sup>3</sup> J. A. McMillan, *Chem. Rev.*, 1962, **62**, 77.

<sup>4</sup> M. Anbar in "Mechanisms of Inorganic Reactions", ed. R. Gould, American Chemical Society, Washington, 1965.