

# Completion of the Pseudocarbonate Series $(C_{2n+2}N_6)^{2-}$ with $n = 1-4$ : Coordination Polymers with new Polynitrile Anions

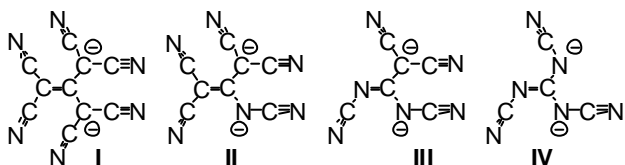
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## Introduction

Due to the -I and -M effect of the nitrile groups the acidic strengths of cyanocarbon acids rival those of the mineral acids<sup>1</sup>. Their corresponding bases, the polynitrile anions, are highly conjugated. The high number of terminal and non terminal nitrogen s-donor atoms, which can coordinate to different metal cations, makes it possible to synthesize coordination polymers of different dimensionalities and unusual magnetic properties<sup>2</sup>. The anions  $(C_{2n+2}N_6)^{2-}$  ( $n = 1-4$ ) are related to carbonate in the sense that one chalcogen atom is substituted by the pseudochalcogens NCN or  $C(CN)_2$ . Exponents I and IV (Fig. 1) of this series of chalcogenide derivatives of carbonate are already known<sup>4,5</sup>. For the first time we now succeeded in synthesizing the two missing links of the pseudocarbonate series, the two cyanocarbonions 2-cyanoimino-1,1,3,3-tetracyanopropandiide,  $(C_8N_6)^{2-}$  (II) and  $N,N',2,2$ -tetracyanoacetamidinate,  $(C_6N_6)^{2-}$  (III) (Fig. 1).



**Figure 1.** The series of the chalcogenide derivatives of carbonate.

Thermolysis of the mercury complexes of these polynitrile anions leads to  $(C_{n+2}N_6)_x$  polymers which allows for a detailed investigation of these amorphous binary networks.

## Results and Discussion

The pseudocarbonate anions  $(C_8N_6)^{2-}$  (II) and  $(C_6N_6)^{2-}$  (III) have been characterized by elemental analyses, IR, Raman and  $^{13}C$ -NMR spectroscopy of their potassium salts, which were prepared in a similar way like described by Middleton et al. for the synthesis of  $Na_2C_{10}N_6$ <sup>4</sup>. The syntheses have to be confirmed under inert conditions but the resulting salts are stable against water and air. The crystal structures of  $[Co(C_8N_6)(C_5H_5N)_4] \cdot (C_5H_5N)$  (1) (Fig. 2) and  $[Cu(C_6N_6)(C_5H_5N)_4]$  (2) (Fig. 3) have been determined by X-ray-diffraction. (1) (monoclinic,  $P2_1/n$ ,  $a=9.7329(3)$ ,  $b=23.2738(8)$ ,  $c=13.7545(4)$  Å,

$\beta=91.327(2)^\circ$ ) can be prepared by metathesis from  $Co(NO_3)_2$  and  $(PPh_4)_2C_8N_6$  in pyridine.



**Figure 2.** Coordination of  $(C_8N_6)^{2-}$  to Co(II) in (1).

(2) (monoclinic,  $C2/c$ ,  $a=16.9268(7)$ ,  $b=18.6169(9)$ ,  $c=16.3383(8)$  Å,  $\beta=94.045(3)^\circ$ ) can be prepared by metathesis from  $CuCl_2$  and  $(PPh_4)_2C_6N_6$  in pyridine.



**Figure 3.** Coordination of  $(C_6N_6)^{2-}$  to Cu(II) in (2).

Both structures are 1 D-polymers with  $\mu_2$  coordinating cyanocarbonions. The octahedral coordination sphere of the Cu(II) cations in (2) is distorted due to the Jahn Teller effect.

## Conclusion

The postulated polynitrile anions  $(C_8N_6)^{2-}$  (II) and  $(C_6N_6)^{2-}$  (III) (Fig. 1) can actually be synthesized and have similar stability like the already known anions  $(C_{10}N_6)^{2-}$  (I) and  $(C_4N_6)^{2-}$  (IV) (Fig. 1) of this series. All four anions form coordination polymers with transition metal cations<sup>2,6</sup>.

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