BIMETALLIC RANDOM CHAINS ; INFLUENCE OF THE PREPARATION PROCEDURE ON
STRUCTURE OF AMORPHOUS $MM'(EDTA)nH_2O$ COMPLEXES

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31000 Toulouse, France***Résumé:**

La structure locale des complexes amorphes $MM'(EDTA)nH_2O$ ($M, M' = Mn, Ni, Co, Cu$) est étudiée par LAXS, mesures magnétiques et spectroscopiques. La structure, similaire à celle de la phase cristallisée, correspond à un empilement en chaînes avec 2 sites alternés pour les métaux M et M'. L'influence de la méthode de préparation sur la structure locale est présentée.

Abstract:

The local structure of the amorphous series $MM'(EDTA)nH_2O$ ($M, M' = Mn, Ni, Co, Cu$) is discussed through LAXS, magnetic and spectroscopic measurements. Similarly to the crystalline phase, this structure shows a chain stacking characterized by alternating environments for the metal ions M and M'. The influence of the preparation procedure on the structure is reported.

I - INTRODUCTION.

The design of new molecular materials with specific physical properties is an area of strong interest in inorganic chemistry. Among studied compounds, low dimensional ones have shown to provide the most significant features when focusing on the correlations structure - magnetic properties /1/.

The aim of this paper is to show how studies of low dimensional amorphous systems allow to acced to further informations on local structure. We report here on the structural characteristics of the amorphous series $MM'(EDTA)nH_2O$ ($M, M' = Mn(II), Ni(II), Co(II), Cu(II)$) investigated by large angle X-ray scattering (LAXS), magnetic and spectroscopic techniques. A special emphasis will be put on the influence of preparation procedures, the origins of the structural disorder, and finally the amount of disorder.

II - INFLUENCE OF THE SYNTHESIS PROCEDURES.

The molecular complexes formulated as $MM'(EDTA)nH_2O$ (hereafter abbreviated as $[MM']$) can be prepared from appropriate synthesis in crystalline /2/ or amorphous states /3/, this last being to its turn isolated as vitreous platelets or powdery solids.

A - The vitreous variety.

Local structure investigations were performed for $[\text{NiNi}]$ and $[\text{CoNi}]$ amorphous complexes by LAXS technique. These allow to emphasize the great similarities between frameworks of amorphous and crystalline complexes. In particular we notice :

- (i) the identical short range order, with the EDTA showing the same coordination scheme.
- (ii) the chain spreading as in the crystalline state (Fig.1)

Fig.1- Structure of $\text{MM}'(\text{EDTA})6\text{H}_2\text{O}$

The only noteworthy difference is the existence of a bond angle distribution between connected ions so that the amorphous complexes can be viewed as made of "flexible" chains.

B - The powdery variety.

Let us now compare the structure of the $[\text{NiNi}]$ powdery variety investigated by LAXS with that of the vitreous one. It may be noticed that both materials exhibit similar radial distribution functions with peaks roughly centered at the same values of r (Fig.2). A thorough examination shows that these peaks are in fact slightly shifted, around $0.1 \text{ \AA}$ for the peaks located between $1.5 - 3 \text{ \AA}$ and up to $0.4 \text{ \AA}$ for those centered at $5.5 - 7 \text{ \AA}$. As previously reported, the former arise from interatomic distances within metal coordination polyhedra whereas the peaks around $5.5 - 7 \text{ \AA}$ are mainly due to intermetallic distances within the chains (in the crystalline state the metal-metal distances are $\text{MM}' = 5.6 - 5.9 \text{ \AA}$ and $\text{M}'\text{M}' = 7.4 - 7.6 \text{ \AA}$).

From the above results, it may be assumed that a weak expansion of the coordination polyhedra and an average elongation of the intermetallic distances occur in the powdery variety.

Such an assumption is supported by the results of electronic spectra. The two amorphous varieties show nearly identical spectra resulting from the presence of the same chromophores. The band around 10000 cm^{-1} may be deconvoluted into

two gaussians, centered at 8700 and 10000 cm^{-1} , that are related to the ${}^3A_2 \rightarrow {}^3T_{2g}$ transition for the $[\text{NiO}_6]$ and $[\text{NiN}_2\text{O}_4]$ chromophores, respectively. Then, we obtain a slight decrease of Dq for the nickel in the "hydrated" position (865 cm^{-1} instead of 877 cm^{-1} for the vitreous sample) while the corresponding value for the "chelated" site remains unchanged. These results allow to underline the quasi-locked conformation of the $[\text{Ni}^{\text{II}}(\text{EDTA})]^{2-}$ moiety, imposed by the rigidity of the EDTA ligand, and conversely the soft framework of the $[\text{Ni}^{\text{II}}\text{O}_2(\text{H}_2\text{O})_4]^{2+}$ unit. Further informations are given by magnetic studies performed in the range 4 - 100K. The temperature dependence of the susceptibility agrees with a power law $\chi = AT^{-\alpha}$ ($\alpha \approx 0.8$) that is the signature of a random exchange-coupled chain. This result confirms the above assumptions from LAXS study.

Fig.2- Comparison of the experimental radial distribution curves for the vitreous and powdery $[\text{NiNi}]$ varieties

The following discussion deals with the structural disorder in the vitreous variety.

III - ORIGIN OF THE DISORDER.

Electronic spectra of the $[\text{CoNi}]$ complex show, in the crystalline state, a selective occupation of $\text{Ni}(\text{II})$ in the "chelated" site in agreement with the largest stability in solution of the $\text{Ni}(\text{EDTA})^{2-}$ anion. Then the thermodynamics warrants the regular sequence $\text{Ni}(\text{II})\text{-Co}(\text{II})\text{-Ni}(\text{II})$ along infinite chains.

Conversely, the structural disorder in amorphous state may arise on one hand from the flexibility of the chains, and on the other hand from a random distribution of metal ions (for $M \neq M'$). The preparation procedure which implies the fast precipitation from an aqueous solution containing the EDTA ligand and the metal ions, allows moreover to control kinetically the occupational order. This way, we have isolated in the bimetallic amorphous system under consideration both $[\text{CoNi}]$ and $[\text{NiCo}]$ chains. Electronic spectra

well agrees with these distinct occupational arrangements ; the observed bands are conveniently assigned to the corresponding chromophores /2/ in figure 3.

Fig.3- Electronic spectra of $[\text{CoNi}]$ and $[\text{NiCo}]$ amorphous complexes

IV - AMOUNT OF DISORDER.

The structural model suggested from LAXS and spectroscopic studies fully agrees with magnetic results. The experimental behavior may satisfyingly be described by means of a Heisenberg chain model, in the classical limit, involving a random distribution of the exchange interactions and alternating magnetic moments. The couplings are assumed to be distributed in order to show a constant value between $J+\lambda$ and $J-\lambda$ and zero otherwise. On account of the very close local structures of the materials under consideration, it appears that λ may be closely related to the amount of structural disorder in each system. For discussing magnetic results, it will be more convenient to use the λ/J ratio that allows to rule out the errors arising from scaling factors /4/. In this way, we have listed in the table the characteristics of the series $[\text{MM}']$.

Note that the sequence coincides with our findings upon the easiness of crystallization of the complexes.

Table : Magnetic parameters of the amorphous complexes.

compounds	J(K)	$\lambda(\kappa)$	$\lambda/ J $	g_a	g_b
[NiNi]	-2.4	7.1	3.0	2.03	2.26
[CoNi]	-3.6	8.0	1.8	4.76	2.10
[CoCo]	-3.8	6.4	1.7	4.76	4.28
[CoCu]	-6.6	8.8	1.3	4.50	2.39
[MnNi]	-3.4	4.2	1.2	2.03	2.53

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References :

- /1/ Miller J. S., "Extended Linear Chain Compounds", vol 3, Plenum Press, New York and London, 1983.
- /2/ Escrivá E., Fuertes A. and Beltrán D., Transition Met. Chem. 9 (1984) 184.
- /3/ Coronado E., Drillon M., Beltrán D. and Bernier J.C., Inorg. Chem. 23 (1984) 4000.
- /4/ Mosset A., Galy J., Coronado E., Drillon M. and Beltrán D., J. Am. Chem. Soc. 106 (1984) 2864.