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The Use of Scanning Electron Microscopy in the Characterization of Coordination Compounds

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Abstract

The use of scanning electron microscopy (SEM) in the study of coordination compounds is reported. The reaction pathways, transmetallation and scrambling reactions, homogeneity, composition and morphology of homo- and heteropolynuclear complexes have been investigated also with the aid of energy dispersive X-ray analysis. A comparison of the results with those obtained with other techniques is also reported.

Introduction

Recently particular attention has been devoted to the preparation of homo- and heterodinuclear or polynuclear complexes owing to the role played by heteropolymetallic centres in many different chemical fields [1–6].

There are many metalloproteins or metalloenzymes that possess functional centres containing two metal atoms held close together, less than 10 Å apart and often less than 5 Å apart [7]. For instance superoxide dismutase, isolated from bovine tissues, is a copper–zinc protein where the bimetallic active site is composed by a square pyramidal copper(II) and a tetrahedral zinc(II) ion linked together by a histidine group. Cytochrome *c* oxidase is a complex enzyme for which the active site is reported to be a copper–iron binuclear complex [9–11].

Studies on the activation of small molecules (especially oxygen) have received a considerable impulse by the use, as activators, of bimetallic complexes [12–14]. The simultaneous presence of two metal ions at a suitable distance to each other represents a requisite for the formation of an activation space necessary for the coordination of oxygen and/or of organic substrates and for their subsequent oxidation. It was found that pairs of clusters of metal ions are sometimes capable of mediating certain chemical reactions either better or in a different way than do isolated centres [12–14].

In order to make the synthesis of these complexes feasible, a series of ligands has been prepared and characterized. Basically five types of ligands can be considered for the classification of binuclear complexes (Scheme 1). Type A are macrocycles, derived from '2 + 2' condensation, type B are side-off acyclic ligands in which a '2 + 1' condensation occurs, type C are end-off acyclic ligands in which a '1 + 2' condensation occurs (in the related metal complexes, Y provides an endogenous bridge; a further exogenous bridge may be provided by a mono- or bidentate anion), type D are polypodal ligands. The chains R and R′ can contain additional donor atoms (NH, S, O, PPh, etc.) producing a multiplicity of different compartments [15, 16]. Compounds A–D have been collectively termed compartmental ligands. Compounds E contain remote chambers; the two macrocycles are constrained in a stacked configuration. Moreover many other types of ligands had to be considered (i.e. ligands in which the compartments are separated by aromatic or similar rings; extendable macropolycycles, etc.); they have been recently reported and classified in review papers [14, 15].

These ligands, by complexation with metals, can give rise to mono or heterobinuclear positional isomers [16]. The complexes have been obtained by addition of the appropriate metal ions to the preformed ligands, but in many cases the template effect was used, especially for the preparation of complexes with not otherwise obtainable ligands [17].

The ligands often have been designed and prepared with coordination sites different enough (in the shape, in the number and/or in the type of donor atoms) to allow the formation of heteropolynuclear complexes. In general the two strategies of 'disymmetric polynucleating ligands' or of 'complexes as ligands' have been used. Sometimes the chemical behaviour of different metal ions favours a hetero-

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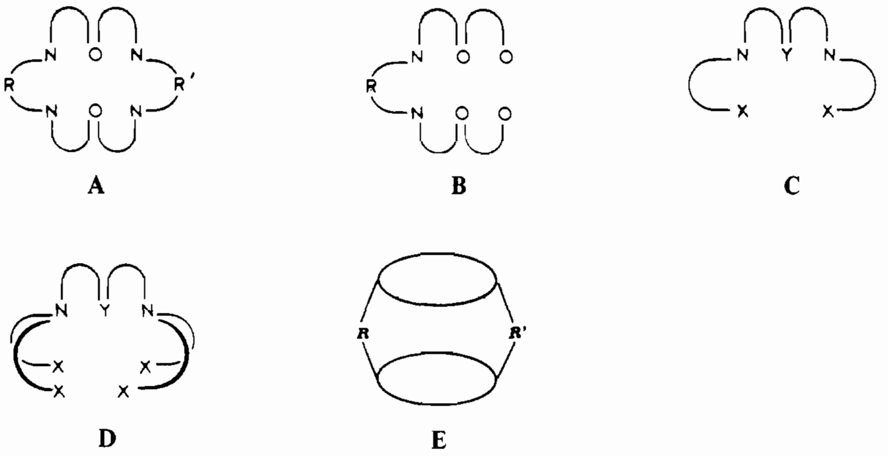


Scheme 1.

nuclear complexation, as obtained for [UO_2Ni(aapen)($dmso)_2$] [18] and [UO_2Cu(aapen)(dmso)] [19] (H_2aapen is the potentially hexadentate Schiff base derived by condensation of *o*-acetoacetylphenol and ethylenediamine in a 2:1 ratio, and contains an inner N_2O_2 chamber and an outer O_2O_2 chamber). The completely different shape of the metal ions together with their markedly different chemical properties does not allow ambiguity; the uranium ion in the external O_2O_2 compartment achieves its preferred seven coordination by adding an equatorial dimethylsulphoxide molecule while the nickel(II) or the copper(II) occupies the inner N_2O_2 chamber. The same heteronuclear complexation to ligands with different chambers occurs also with transition metal ions and several X-ray structures have been reported [11–16].

When symmetric ligands or similar metal ions are used, the preparation of heteropolynuclear complexes becomes more difficult. In these systems a change of coordination site of the metal ions can occur with the consequent formation of homodinuclear complexes in addition to heterodinuclear species according to reactions of the type [20]

$$2[M_aM_bL]^{n+} \longrightarrow [M_aM_aL]^{n+} + [M_bM_bL]^{n+}$$

Heteropolynuclear complexes containing lanthanides, owing to their physicochemical properties, are considered good candidates for the preparation of materials with particular magnetic, electric or optical properties. The physicochemical properties of a sample is obviously correlated to its intimate structure. Unfortunately it is not always possible to grow crystals suitable for X-ray analysis, consequently, the use of different techniques is necessary for a correct study of such properties.

The elemental analyses of the samples can be conveniently obtained by different techniques and the occurrence of heteropolynuclear species can be sometimes inferred by mass spectrometry. A serious limitation of this technique comes from the low volatility of these samples; it is not always easy to obtain good results even by using FAB (fast atom bombardment) mass spectrometry. The metal content can be obtained by atomic absorption or emission which are however destructive analyses and give a picture of the sample as a whole and do not discriminate between homogeneous and/or non-homogeneous complexes. SIMS (secondary ions mass spectrometry) can be also used for fast and sensitive analytical determinations on solid compounds and solutions; it is a destructive analysis which necessitates small quantities of the sample. Moreover it was found that the X-ray fluorescence spectroscopy is useful in characterizing these complexes. By integration of backscattered X-rays, using a scanning electron microscope, metal ratios can be detected and the sample homogeneity checked. This can be a non-destructive technique which gives punctual multi-element analysis (on volumes of about 1 μ^3).

By employing this procedure it is possible to be more certain in the assignment of the physicochemical properties of these systems.

The present paper reports some examples of application of this technique to inorganic compounds and a discussion of the results taking into account the data obtained from the use of the techniques above mentioned.

Experimental

The preparation of the complexes reported in the present paper has been already published [21–25].

All the observations were made with a Philips SEM 505 model scanning electron microscope equipped with an EDAX Model Data Station. Metal ratios were conveniently determined by the integral counting of back-scattered X-ray fluorescence radiation. Samples suitable for SEM analysis, were prepared by suspending the microcrystalline powders in petroleum ether 30–40. Some drops of the resulting suspension were placed on a graphite plate and after evaporation of the solvent the samples were metallized with gold or graphite by using an Edward's S150 model sputter coater [26].

Three types of detectors have been used for the investigations on our samples:

(i) secondary electrons detector (for morphology)

(ii) X-rays detector (for energy dispersive spectrometry)

(iii) backscattered electrons detector (for a qualitative view of the heavy atoms distribution in the samples.

The instrumental response on the ratio of the elements in a sample depends on the morphology and the orientation of the microcrystals. These data depend also on the accelerating voltage applied on the electron gun.

The use of standards is needed in order to obtain a good reproducibility of the analyses. We used, as standards, crystals of complexes with the same or with similar ligands and containing the same metals of the observed sample. As the properties and the molecular structures of the reference complexes are known (and obviously the metal content) it is possible to vary the observation conditions (accelerating voltage, orientation of the specimen, spot dimension, etc.) to obtain the same result in the energy dispersive X-ray analyses.

The correct metal content of the reported complexes has been determined by atomic absorption or (for lanthanide complexes) by emission, using a Varian AA-275 Atomic Absorption Spectrophotometer. The same metal content and metal/metal ratio in the heterobinuclear lanthanide(III) complexes has also been established by a new procedure using the SIMS technique [27, 28].

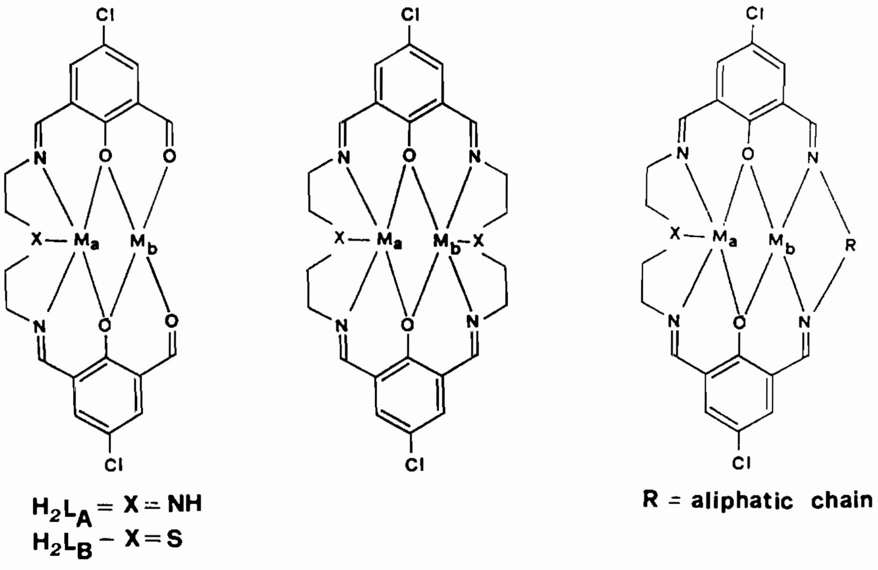
Results and Discussion

Homogeneity of Heteropolynuclear Complexes

The difficulty in the preparation of heterodinuclear complexes owing to scrambling reactions of the type reported in the introduction, can be partially overcome by employing, in some cases, the following procedure. The addition of the appropriate M_b(II) salt to a suspension of the acyclic complex M_a(II)L in methanol results in the rapid complexation of M_b(II) to the vacant O_2O_2 site. For the preparation of the related cyclic complex the subsequent condensation of the appropriate polyamines to the free carbonyl groups of the acyclic ligand is necessary.

As an example, heterodinuclear complexes with macrocyclic and symmetric or asymmetric macrocyclic ligands, obtained by condensation of 2.6-diformyl-4-chlorophenol and facultative diamine (1,5-diamino-3-azapentane, 1,5-diamino-3-thiapentane and aliphatic diamines) also by using the template effect, are reported in Scheme 2.

Provided that the time in solution is short and the temperature is too low to surmount the activation barrier for dissociation, little scrambling has been observed.



Scheme 2.

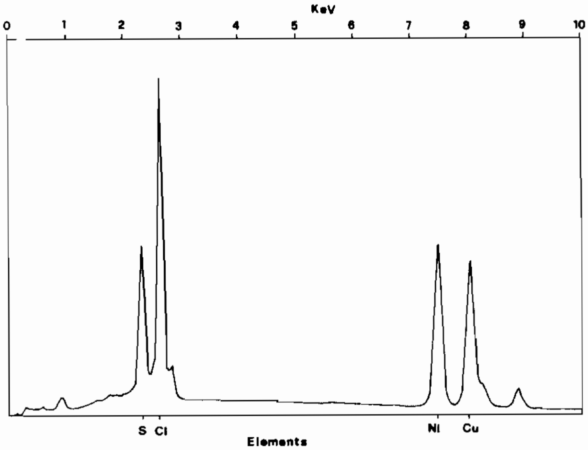
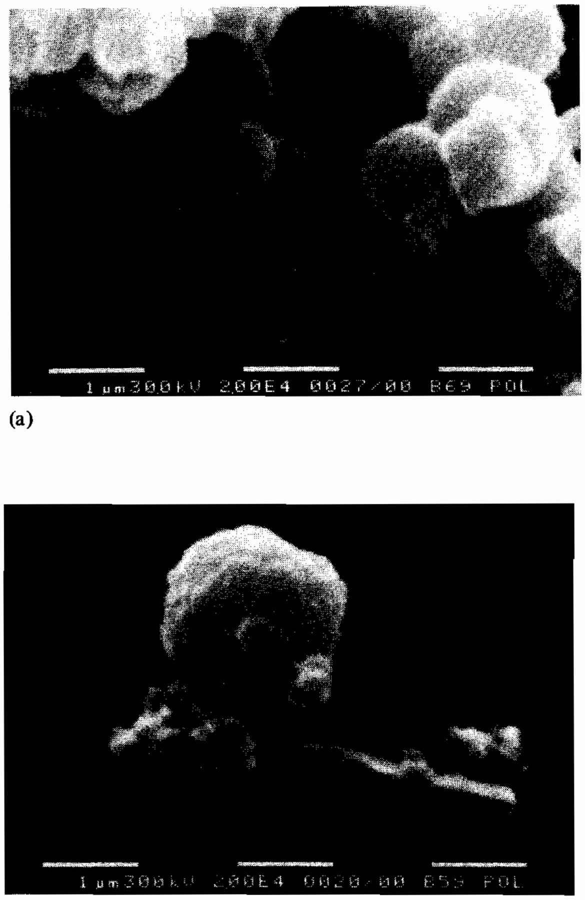


Fig. 1. X-ray fluorescence spectrum of $[CuNiL_B(OAc)_2] \cdot 2H_2O$.



(a)

(b)

Fig. 2. (a) Photograph of $[CuNiL_B(OAc)_2] \cdot 2H_2O$ (microcrystalline powders of about 1 μ^3 size). (b) Photograph of a sample formulated as $[CuNiL_B(Cl)_2] \cdot H_2O$ (the presence of two different components is easily detectable).

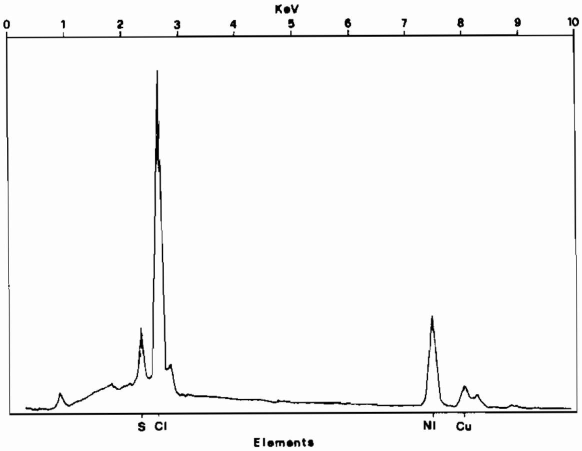


Fig. 3. X-ray fluorescence spectrum of the globular particle in the upper part of Fig. 2b.

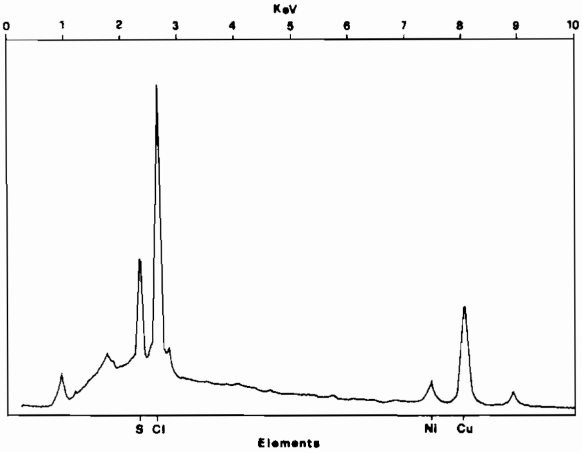


Fig. 4. X-ray fluorescence spectrum of the crystal in the lower part of Fig. 2b.

X-ray fluorescence spectroscopy has given the ratios of heavy atoms contained in the compounds under investigation. As an example, for the complex $CuNiL_B(OAc)_2 \cdot 2H_2O$ (Fig. 1), it shows the S, Cl, Ni, and Cu ratios are qualitatively 1:2:1:1, as confirmed, within the standard deviations, by electron microprobe analyses.

$CuNiL_B(OAc)_2 \cdot 2H_2O$ is a homogeneous microcrystalline powder of about 1 micron size (Fig. 2(a)); on contrary samples like that in Fig. 2(b), given on the basis of elemental analyses as $CuNiL_BCl_2 \cdot 3H_2O$, must be discharged owing to different morphologies and different X-ray fluorescence patterns of the two species contained in the product (Fig. 3 and Fig. 4).

The globular particle (top in Fig. 2b) contains a high percentage of nickel with respect to the percentage of copper, while the crystal (bottom in

Fig. 2b) has a high percentage of copper with respect to the percentage of nickel. By this procedure a series of metal complexes with the above ligands have been selected and their structural, magnetic, electrochemical and optical properties correctly determined [24, 25].

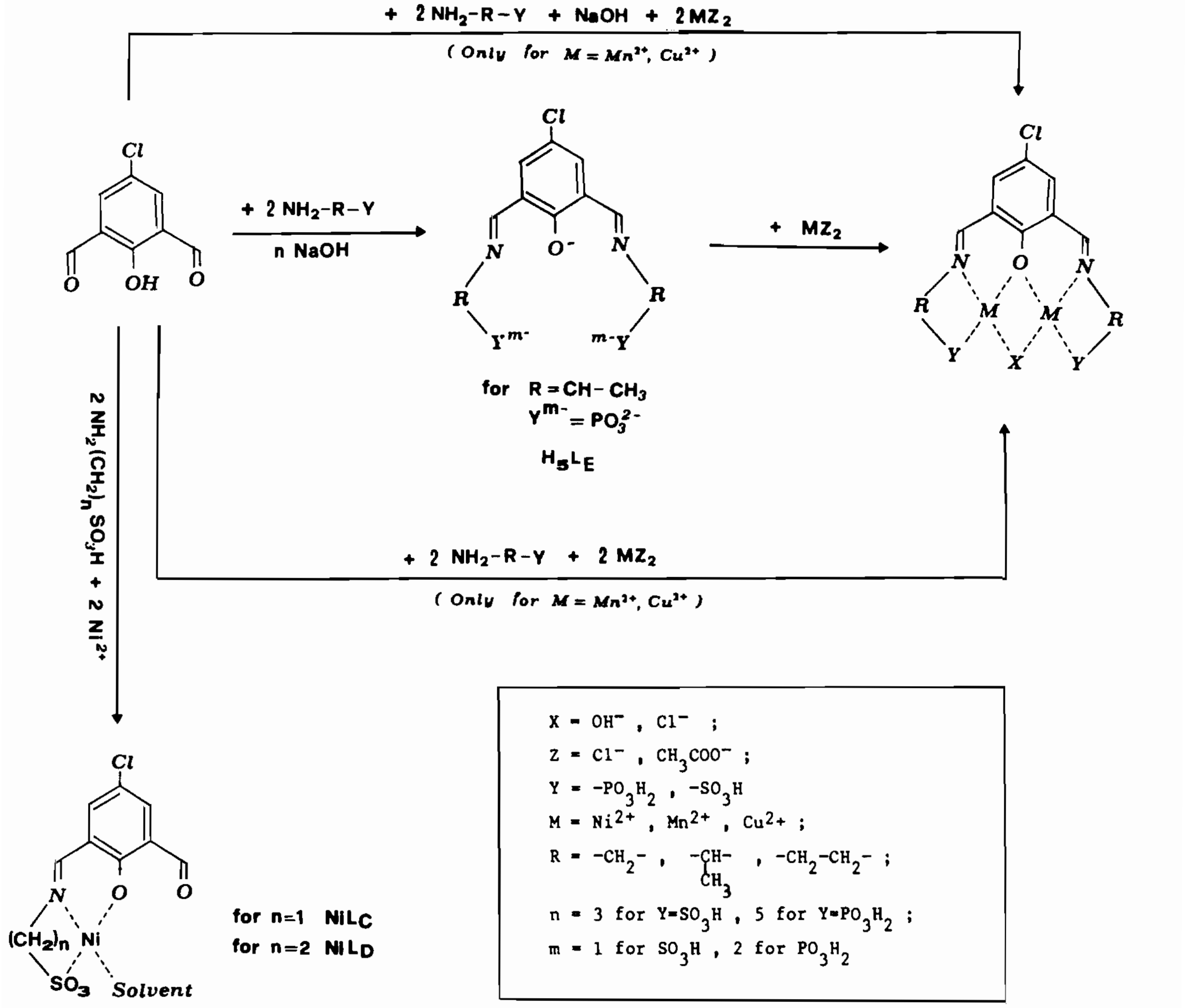
Reaction Pathways

It is possible to obtain information on reaction pathways. For instance the formation of mono- or homobinuclear complexes has been proposed in the reaction of nickel(II), manganese(II) and copper(II) salts with the compartmental ligands derived from 2,6-diformyl-4-chlorophenol and α or β-aminosulphonic or phosphonic acids [24, 25] (Scheme 3).

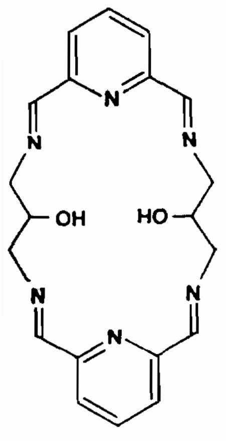
Physicochemical data suggest that nickel(II) gives, by the template procedure, the complexes $NiL_C \cdot 2H_2O$ and $NiL_D \cdot 2.5H_2O$ and by reaction with the preformed ligand $Na_5L_E \cdot 3H_2O \cdot 2CH_3OH$, the complex $Na_2Ni_2L_EOH \cdot 3H_2O \cdot 2CH_3OH$ [13]. From SEM data the metal, chlorine, sulphur (or phosphorus) and sodium ratios, when present, and the sample homogeneity were confirmed for all the prepared complexes [13]. As an example the X-ray fluorescence spectra of the binuclear complexes of nickel(II), $Na_2Ni_2L_EOH \cdot 3H_2O \cdot 2MeOH$, and manganese(II), $Na_2Mn_2L_EOH \cdot 2MeOH$, with H_5L_E show Na, P, Cl, Ni or Mn ratios are qualitatively 2:2:1:2, again confirmed, within the standard deviations, by electron microprobe analyses.

The reaction of 1,3-diamino-2-hydroxypropane with 2,6-diacetylpyridine in the presence of BaX_2 (X = perchlorate or thiocyanate) led to the preparation of complexes $[Ba(H_2L_F)X_2]$.

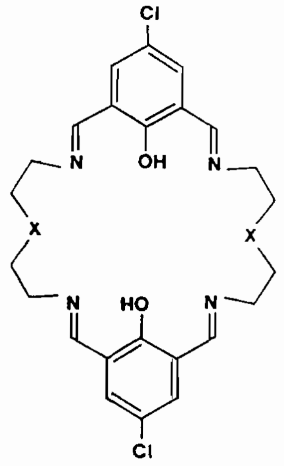
The analysis of $Ba(H_2L_F)(SCN)_2$ revealed that in addition to this complex there is a minor product to



Scheme 3.



H_2L_F



H_2L_G X = NH
H_2L_H X = S

be described as $Ba(L_F)$ without thiocyanate groups where the macrocycle has probably lost the two hydroxylic protons.

Transmetallation Reactions

SEM has been used also in the study of transmetallation reactions. A transmetallation via the formation of a heterobinuclear species was observed in the reaction

$$NiL_B + CuCl_2 \xrightarrow{MeOH} NiCuL_BCl_2 \xrightarrow{dmf} CuL_B + NiCl_2$$

The three complexes have also been well characterized by X-ray diffractometry. X-ray fluorescence microprobe analysis has given useful information about the composition and the homogeneity of the three different compounds [21].

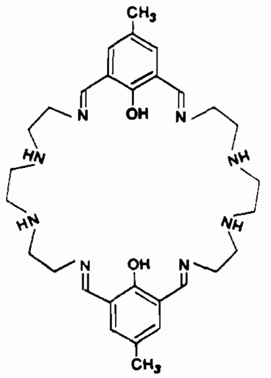
Recently we have prepared a series of lanthanide complexes of the types $[Ln(H_2L_G)(NO_3)_2](NO_3)$ and $[Ln(H_2L_H)(NO_3)_2](NO_3)$. In the complexes $[Ln(H_2L_G)(NO_3)_2](NO_3)$ (Ln = Eu, Tb) a ring contraction occurs in the chamber not involved in the coordination to the lanthanide ion; this allows a contraction of the central cavity and a reduction in ligand denticity. In the terbium or in the isostructural europium complexes [23] the metal ion is nonacoordinate, being bound to five donor atoms from the cyclic polydentate ligand and to four oxygen atoms of two bidentate nitrate groups, the third nitrate being ionic (Fig. 5).

These complexes contain a chamber free for a further coordination. Reaction of these complexes with $Cu(OAc)_2$ or $Zn(OAc)_2$ produces the mononuclear copper(II) or zinc(II) analogues as final products. Intermediate samples containing both metal ions have also been determined (Figs. 6–9).

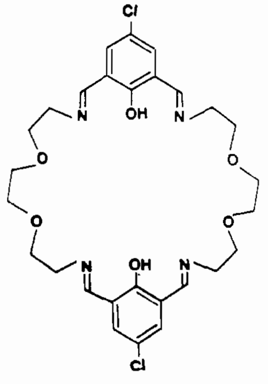
Again a transmetallation reaction takes place, a heterobinuclear species, being the intermediate complex.

Vicariancy and Formation of Isostructural Compounds

Recently the synthesis of homodinuclear lanthanide complexes with the large binucleating macrocyclic ligand (H_2L_I) obtained by condensation of 2,6-diformyl-4-methylphenol and triethylenetetramine, has been reported [29]. With the aim of studying the interactions between lanthanide ions and to avoid possible ring contractions, as seen for the complexes containing a –NH group in the side chain of the ligand, we have synthesized the macrocycle H_2L_L by reaction of the keto-precursor 2,6-diformyl-4-chlorophenol and the polyamine 1,8-diamino-3,5-dioxaoctane. The FAB mass spectrum of H_2L_L shows the parent peak at the expected m/z value with a pattern consistent with the presence of chlorine atoms.



H_2L_I



H_2L_L

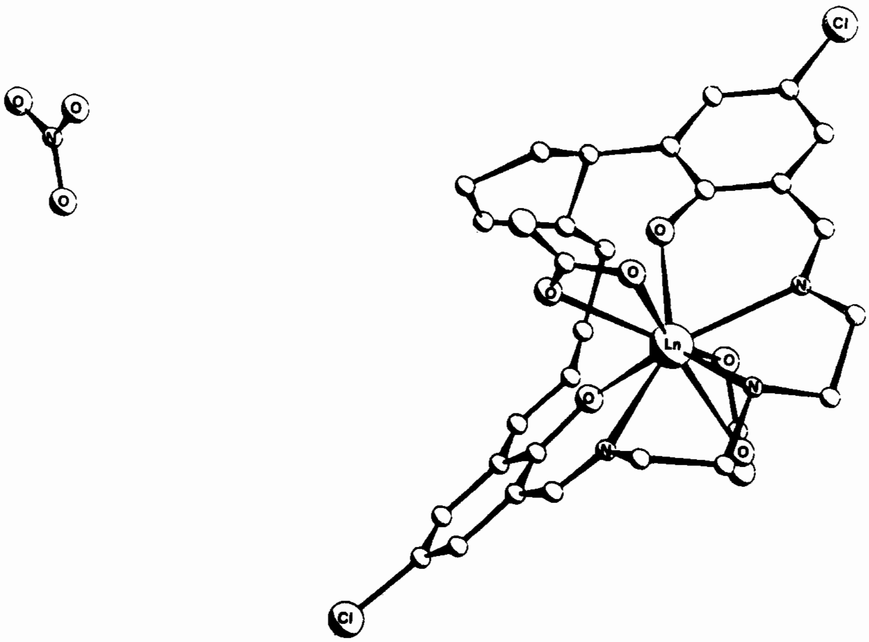


Fig. 5. Crystal structure of $[Ln(H_2L_G)(NO_3)_2]NO_3$ (Ln = Eu, Tb).

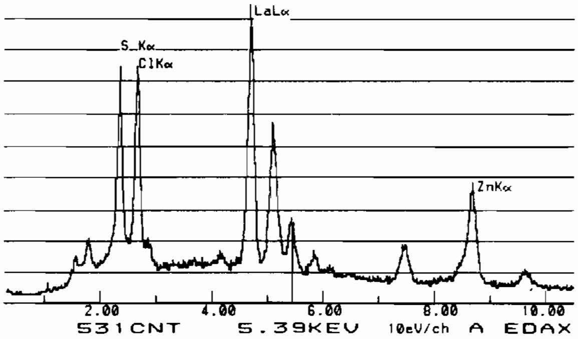


Fig. 6. X-ray fluorescence spectrum of the La–Zn intermediate in the transmetallation reaction of $[La(H_2L_G)(NO_3)_2]NO_3$ with $Zn(OAc)_2$.

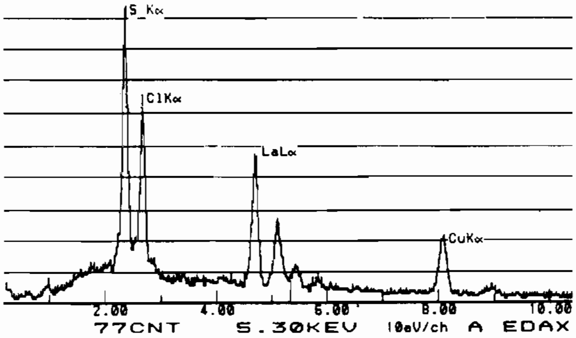


Fig. 8. X-ray fluorescence spectrum of the La–Cu intermediate in the transmetallation reaction of $[La(H_2L_G)(NO_3)_2]NO_3$ with $Cu(OAc)_2$.

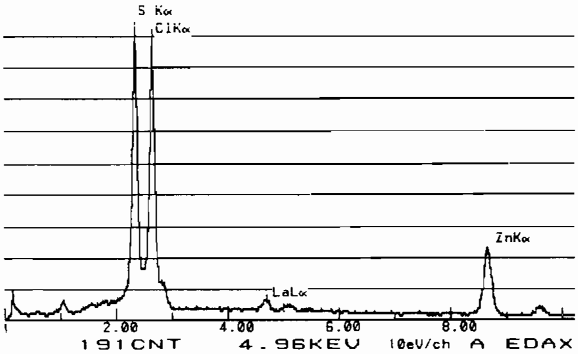


Fig. 7. X-ray fluorescence spectrum of the final zinc product derived from the transmetallation reaction of $[La(H_2L_G)(NO_3)_2]NO_3$ with $Zn(OAc)_2$.

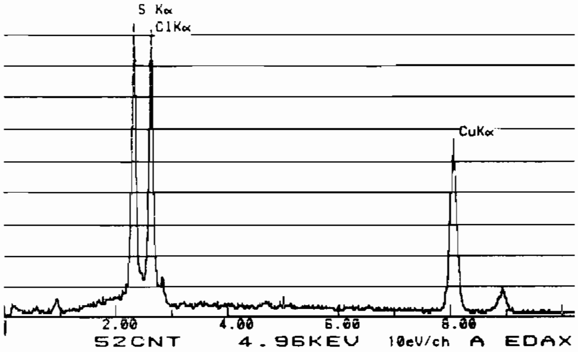


Fig. 9. X-ray fluorescence spectrum of the final copper product derived from the transmetallation reaction of $[La(H_2L_G)(NO_3)_2]NO_3$ with $Cu(OAc)_2$.

With this macrocyclic ligand H_2L_L, complexes formulated as $Ln_2L_L(NO_3)_4 \cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, Dy; $n = 1, 2$) and $Ln^1{}_x{-}Ln^2{}_{(2-x)}L_L(NO_3)_4 \cdot nH_2O$ ($Ln^1{-}Ln^2$ = La–Sm, La–Gd, La–Dy, La–Eu, Dy–Gd, Dy–Eu, Gd–Eu; $n = 1, 2$) have been obtained.

FAB mass spectra of lanthanum and terbium samples were obtained. The pseudomolecular ions were not observed but the spectra gave strong evidence for the presence of a binuclear species: in fact, abundant peaks attributable to $M^+ - NO_3$, $M^+ - Ln(NO_3)_2 + 2H^+$, $M^+ - Ln(NO_3)_3 + H^+$ and $M^+ - Ln(NO_3)_4$ were detectable. For the terbium complex the species exhibited the relative aboundance patterns due to the presence of Cl and Tb.

The homodinuclear complexes are microcrystals, 5–10 μm long and 0.5 μm thick, where the chloride/lanthanide ratio is 1:1, within the standard error, in agreement with elemental analysis. As an example the Gd–Gd complex (Figs. 10 and 11) appears as a homogeneous microcrystalline powder with a Gd:Cl ratio approximately 1:1.

The powders of the heterobinuclear complexes are homogeneous microcrystals with the expected $Ln^1/Ln^2/Cl$ ratio = 1:1:2. As an example the La–Sm and the La–Eu microcrystalline powders give the results reported in the Figs. 12 and 13.

Crystals of La–Sm grown from the mother liquor, again have a lanthanide/chlorine 1:1 ratio, but the content of samarium is about four times that of lanthanum. Punctual analysis over the whole specimen (Figs. 14–17) shows that the distribution of the two metals in the various crystals is homogeneous, suggesting a stoichiometry of the type $Sm_{1.6}La_{0.4}L_L(NO_3)_4$. A similar behaviour was found for the

Fig. 10. A photograph of microcrystals of the complex $[Gd_2(L_L)(NO_3)_4] \cdot H_2O$.

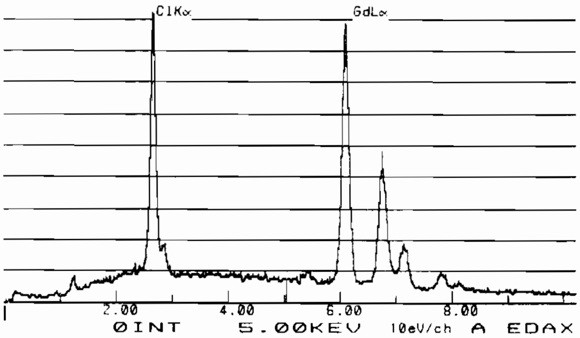


Fig. 11. X-ray fluorescence spectrum of a microcrystal of the complex $[Gd_2(L_L)(NO_3)_4] \cdot H_2O$.

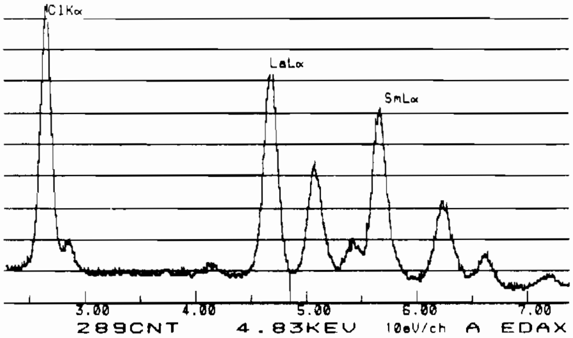


Fig. 12. X-ray fluorescence spectrum of microcrystals of the complex $[La{-}Sm(L_L)(NO_3)_4] \cdot H_2O$.

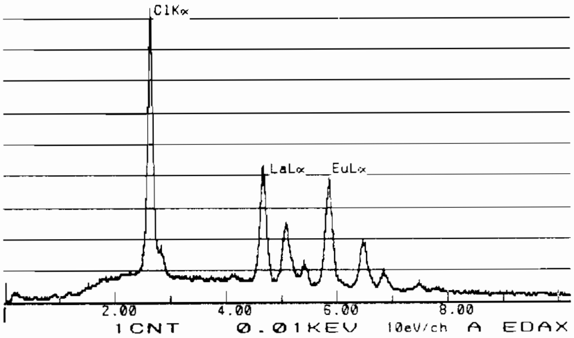


Fig. 13. X-ray fluorescence spectrum of microcrystals of the complex $[La{-}Eu(L_L)(NO_3)_4] \cdot H_2O$.

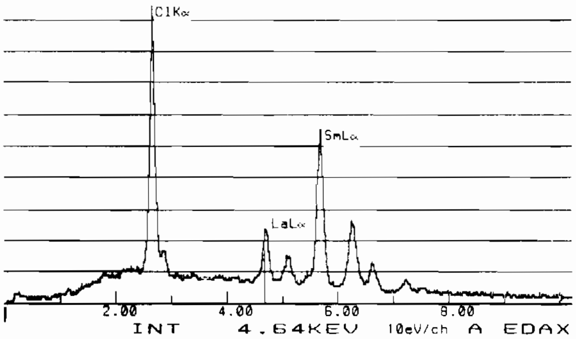


Fig. 14. X-ray fluorescence spectrum of crystals of the complex formulated as $[La_{0.4}{-}Sm_{1.6}(L_L)(NO_3)_4] \cdot H_2O$.

Fig. 15. A photograph of crystals of the complex formulated as $[La_{0.4}-Sm_{1.6}(L_L)(NO_3)_4]\cdot H_2O$.

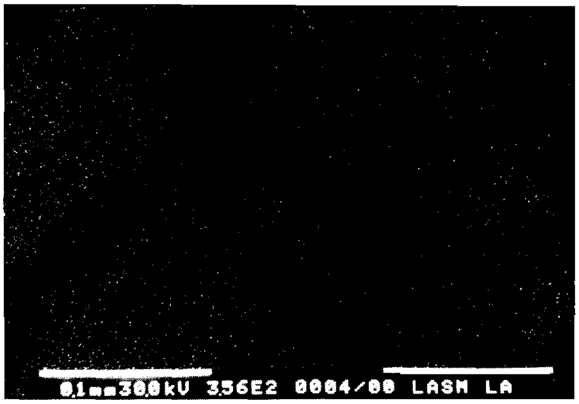


Fig. 16. A map of the distribution of lanthanum in the crystals of the complex formulated as $[La_{0.4}-Sm_{1.6}(L_L)(NO_3)_4]\cdot H_2O$ shown in Fig. 15.

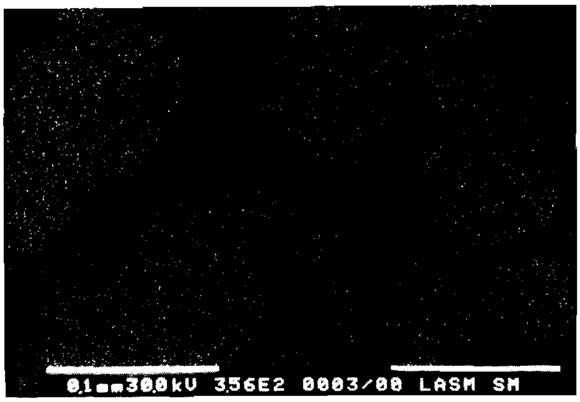


Fig. 17. A map of the distribution of samarium in the crystals of the complex formulated as $[La_{0.4}-Sm_{1.6}(L_L)(NO_3)_4]\cdot H_2O$ shown in Fig. 15.

crystals containing La and Dy also grown from the mother liquor; the dysprosium content is about a tenth of lanthanum.

Analyses on the microcrystalline powders of $Ln^1Ln^2L_L(NO_3)_4$ are in line with the elemental analyses and give a $Ln^1/Ln^2/Cl$ atomic ratio = 1:1:2. According to these data, the formation of heterodinuclear species can be proposed. The same results have been obtained by employing the SIMS technique [28].

The morphology of the samples shows a lamellar structure. X-ray powder patterns for several different samples, containing homo- or heterodinuclear lanthanide complexes, show they are all isostructural. This is a reasonable result, because the chemical properties of the various lanthanides(III) are very similar and their ionic radius varies from 1.15 (La(III)) to 0.93 (Lu(III)) Å. Thus it is easy to find in the mother liquors compounds with a very different ratio between the two lanthanides maintaining the same structure.

Conclusions

Scanning electron microscopy together with scanning electron microprobe analysis has given useful information on the morphology and composition of heteropolynuclear complexes, allowing a more definite understanding of the physicochemical properties of these samples. Moreover, this technique aids in the discard of the number of impure samples preparation without resorting to more time consuming and expensive analytical procedures [20].

It is obvious that optical, magnetic, spectroscopic, mass spectrometry data etc., are necessary for a correct identification of these complexes, but these techniques do not give the necessary certain information for the knowledge of the intimate structure. X-ray diffractometry has the obvious limitation that it is not always possible to grow crystals suitable for such an investigation.

In this context the information coming from other techniques (ESCA, Auger, SIMS, FAB, etc.), in addition to the electron microscopy technique reported here, can give the complete and correct picture of the chemical situation in the samples prepared.

Acknowledgement

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References

1 O. Kahn, *Struct. Bonding (Berlin)*, *68* (1987) 89.
2 R. D. Willet, D. Gatteschi and O. Kahn, *Magneto-structural Correlations in Exchange Coupled Systems*, D. Reidel, Dordrecht, 1985.

3 K. D. Karlin and J. Zubieta, *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives,* Adenine, New York, 1983.

4 K. D. Karlin and J. Zubieta, *Biological and Inorganic Copper Chemistry,* Vols. 1 and 2, Adenine, New York, 1986.

5 M. Haneck, A. Detz, R. Fay, K. Fischer, U. Keppeler, J. Koch, J. Metz, M. Metzger, O. Schneider and H.-J. Schulze, in T. A. Skotheim (ed.), *Handbook of Conducting Polymers,* Vol. 1, Marcel Dekker, New York, 1986, p. 133.

6 J. S. Miller, Extended Linear Chain Compounds, Vols. 1, 2 and 3, Plenum, New York, 1982 and 1983.

7 P. J. Sadler, *Inorg. Perspect. Biol. Med., 1* (1978) 233.

8 J. S. Richardson, K. A. Thomas, B. H. Rubin and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A., 72* (1975) 1349.

9 M. Erecinska and D. F. Wilson, *Arch. Biochem. Biophys., 1* (1978) 188.

10 D. C. Warthon, in G. L. Eichhorn (ed.), *Inorganic Biochemistry,* Elsevier, Amsterdam, 1973, Ch. 27.

11 R. A. Scott, S. P. Cramer, R. W. Shaw, H. Bernert and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A., 78* (1981) 664.

12 K. Karlin and Y. Gultneh, in S. J. Lippard (ed.), *Progress in Inorganic Chemistry,* Vol. 35, Wiley, New York, 1987, p. 219.

13 P. A. Vigato, S. Tamburini and D. E. Fenton, *Coord. Chem. Rev.,* submitted for publication.

14 D. E. Fenton, in A. G. Sykes (ed.), *Advance in Inorganic and Bioinorganic Mechanism,* Vol. 2, Academic Press, London, 1983, p. 187.

15 P. Zanello, S. Tamburini, P. A. Vigato and G. Mazzocchin, *Coord. Chem. Rev., 77* (1987) 165.

16 U. Casellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev., 8* (1979) 199.

17 D. E. Fenton, S. J. Kitchen, C. M. Spencer, S. Tamburini and P. A. Vigato, *J. Chem. Soc., Dalton Trans.,* (1988) 685, and refs. therein.

18 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Met. Chem., 3* (1978) 99.

19 R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Transition Met. Chem., 3* (1978) 239.

20 R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc., 103* (1981) 4073.

21 U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 119* (1986) 215.

22 E. Bullita, U. Casellato, P. Guerriero and P. A. Vigato, *Inorg. Chim. Acta, 139* (1987) 59.

23 P. Guerriero, U. Casellato, S. Tamburini, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 129* (1987) 127.

24 P. Guerriero, U. Casellato, D. Ajo, S. Sitran, P. A. Vigato and R. Graziani, *Inorg. Chim. Acta, 142* (1988) 305.

25 P. Guerriero, D. Ajo, P. A. Vigato, U. Casellato, P. Zanello and R. Graziani, *Inorg. Chim. Acta, 141* (1988) 103.

26 A. Armigliato and U. Valdré, *Microscopia elettronica a scansione e microanalisi,* Vols. 1 and 2, Università di Bologna, Centro Stampa Lo Scarabeo, Bologna, 1980.

27 S. Daolio, B. Facchin and C. Pagura, *Int. J. Mass. Spectrom. Ion Proc., 76* (1987) 277.

28 S. Daolio, E. Bullita, B. Facchin, P. Guerriero, C. Pagura and P. A. Vigato, *Workshop on Basic and Applied Aspects of Rare Earths, Venice, Italy, May 26–27, 1988,* p. 25.

29 I. A. Kahwa, J. Selbin, T. C.-Y. Hsieh and R. A. Laine, *Inorg. Chim. Acta, 118* (1986) 179.