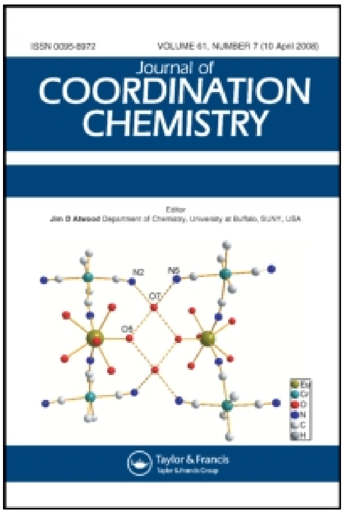

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COMPLEXES OF MOLYBDENUM(V) AND LANTHANUM(III) WITH 2',2'''-(2,6-PYRIDINEDIYLDIETHYLIDENE)-DIOXAMOHYDRAZIDE (H_2DAPSOX)

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COMPLEXES OF MOLYBDENUM(V) AND LANTHANUM(III) WITH 2′,2‴-(2,6-PYRIDINEDIYLDIETHYLIDENE)-DIOXAMOHYDRAZIDE (H_2DAPSOX)

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In a template synthesis from ethanolic solution of $MoOCl_3$, 2,6-diacetylpyridine (dap), and semioxamazide (sox), in the molar ratio 1 : 1 : 2, a dimeric molybdenum(V) complex $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ (where H_2dapsox = 2′,2‴-(2,6-pyridinediyldiethylidenedioxamohydrazide) was obtained. In a similar reaction, starting from $La(NO_3)_3 \cdot 6H_2O$, the complex $[La(H_2dapsox)(NO_3)_x](NO_3)_{3-x} \cdot 1/2EtOH$ ($x = 1, 2$), having coordination number 9, was obtained. In the latter complex two NO_3 groups were bidentately coordinated in the solid state, but only one in the solution.

Besides $[Mo_2O_2(TPP)_2]$ (TPP = tetraphenylporphyrin), the molybdenum(V) complex $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ is the only other known example of a dimeric μ-oxodimolybdenum(V) species that is paramagnetic ($\mu = 0.95$ BM). One of the Mo atoms has pentagonal bipyramidal coordination, and the other pentagonal pyramidal coordination. In aqueous solution a rare example of a pentagonal pyramidal ion $[MoO(dapsox)]^+$ is presumably present. Solution EPR spectra (at 77 K) cannot be related to either of the two known types of Mo(V) species based on the extent of g anisotropy. The substances also were characterized by IR and electronic spectroscopy, and by thermal analysis.

Keywords: Molybdenum(V); Lanthanum(III); Multidentate complexes; Polydentates

INTRODUCTION

Previous work [1–4] has focused on the investigation of 3*d*-metal complexes with the H_2dapsox ligand and its deprotonated forms. Since H_2dapsox was

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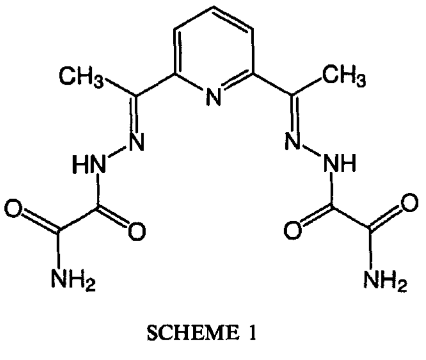
*Corresponding author.

found to be particularly fitted to form a PBP coordination sphere around 3*d*-metals, it was of interest to determine the coordination and geometry of its complexes with ions that have a greater radius. To that end, we have characterized the corresponding UO_2^{2+} complex [5]. Here we present results obtained for MoO^{3+} and La^{3+} complexes.

Among μ-oxo dimers of biological importance, molybdenum(V) dimers are notable examples. The chemistry of molybdenum(V) is dominated by dimeric species, and studies of monomeric Mo(V) complexes, conditions under which they are stable, and their structural characterization provide useful information for the elucidation of the role of molybdenum in enzymes [6]. Dimeric complexes containing $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$ units are among the most common with either *cis* or *trans* orientation of the terminal Mo—O bonds. Perpendicular orientation of the bonds is not known, but a linear orientation is present, to our knowledge, only in a tetraphenylporphyrinato dimer of Mo(V) [7, 8]. These structural features are related to the fact that Mo(V) μ-dioxo dimers are exclusively diamagnetic. Paramagnetism could be expected only in the case of a skew arrangement of the terminal Mo—O bonds (dihedral angle of 90°) but such structures have not been characterized so far. Bending of the Mo—O—Mo bridge, detectable by IR spectroscopy [9], may also contribute to paramagnetism. The only known example of a paramagnetic complex having a linear O=Mo—O—Mo=O fragment is the $[Mo_2O_3(TPP)_2]$ dimer [7].

This work originated in our search for other possible paramagnetic μ-oxo-dimolybdenum(V) complexes that might be of interest in the investigations of molybdenum enzyme systems. A suitable ligand system for this goal proved to be an acyclic multidentate acylhydrazone, H_2dapsox (Scheme 1), which can coordinate in an asymmetrical quadridentate or symmetrical quinquedentate mode depending on the nature of the central metal atom



SCHEME 1

[1–4]. The extended system of conjugated double bonds in H_2dapsox enabling a high π-electron delocalization in the ligand xy-plane contributes to the high planarity of this ligand. Furthermore, the fact that H_2dapsox is not a macrocyclic ligand enables the metal atom to remain coplanar with the ligating atoms. In contrast, porphyrin macrocycles in analogous TPP complexes [10] deviate from planarity much more. All these features make structures with H_2dapsox interesting and worth studying with respect to ligand deprotonation, interaction between Mo(V) atoms, and stabilities in the solid and in solution, in comparison to analogous monomeric complexes.

EXPERIMENTAL SECTION

$[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$

Forty milliliters of absolute ethanol were poured over 0.18 g (0.5 mmol) of finely powdered K_2MoOCl_5. After 5 hours the resulting precipitate (KCl) was filtered off. To the filtrate (the ethanolic $MoOCl_3$ solution) 0.08 g (0.5 mmol) of dap and 0.1 g (1 mmol) of sox was added. The reaction mixture was refluxed with stirring for about 3 hours, whereupon a dark (black) microcrystalline precipitate was obtained. After removing the filtrate, the precipitate was washed with ethanol. The whole procedure was repeated in an N_2 atmosphere with identical results. Yield: 78%. Molar conductance (Λ_M; $\Omega^{-1}cm^2mol^{-1}$): 497. *Anal.* Calc. for $C_{26}H_{38}Cl_6Mo_2N_{14}O_{14}$(%): C, 26.55; H, 3.23; N, 16.18. Found: C, 26.32; H, 3.65; N, 16.09. Solid state $\mu_{eff.} = 0.95$ BM; aqueous solution $\mu_{eff.} = 1.82$ BM. IR (KBr pellet; ν (cm^{-1})) 3445(s), 3293(s), 3242(s), 1690(vs), 1591(s), 1568(s), 1530(m), 1453(m), 1401(m), 1322(m), 1295(s), 1195(s), 1065(w), 1022(w), 915(m), 815(w), 680(s), 504(w).

$[La(H_2dapsox)(NO_3)_2]NO_3 \cdot 1/2EtOH$

An ethanolic suspension containing 0.20 g (1.2 mmol) of dap, 0.24 g (2.4 mmol) of sox and 0.52 g (1.2 mmol) of $La(NO_3)_3 \cdot 6H_2O$ was heated for about 3 hours under reflux. A white-yellow microcrystalline product was obtained and was separated by filtering. Yield: 53%. Molar conductance (Λ_M; $\Omega^{-1}cm^2mol^{-1}$): 134. *Anal.* Calc. for $C_{14}H_{18}La_1N_{10}N_{14}O_{13.5}$(%): C, 24.67; H, 2.64; N, 20.56. Found: C, 24.32; H, 2.93; N, 20.21. IR (KBr pellet; ν (cm^{-1})) 3471(s), 3337(s), 3251(s), 2331(w), 1721(s), 1676(vs), 1626(m), 1584(m), 1538(s), 1494(s), 1451(vs), 1385(vs), 1304(vs), 1254(m), 1223(m), 1197(m), 1152(w), 1129(w), 1070(w), 1041(m), 1006(m), 943(w), 822(m), 738(m), 656(m), 618(m), 591(m), 493(m), 445(w), 419(w), 405(w).

Physical Measurements

Molar conductivity was measured at room temperature (1×10^3 mol dm^{-3} solution in DMF) on a Jenway 4009 digital conductivity meter. IR spectra were recorded on a Perkin Elmer FTIR 1726 spectrophotometer. Electronic spectra were recorded for 1×10^{-3} mol dm^{-3} aqueous solutions on a GBC UV/VIS 911-A spectrophotometer. Thermal analyses (TG, DTG, DSC) were performed in inert atmosphere (of N_2) on a Du Pont 9900 instrument equipped with a model 910 differential scanning calorimeter and a model 951 thermogravimeter. The heating rate was 10° min^{-1}. Solid state magnetic moments were measured at 291 K using an MSN–MK1 balance from Sherwood Scientific Ltd., and were corrected for diamagnetism. Magnetic moments were determined in solution using the Evans method [11]. X-band EPR spectra of solutions at 293 K and 77 K were obtained using a Varian E-104A EPR spectrometer.

RESULTS AND DISCUSSION

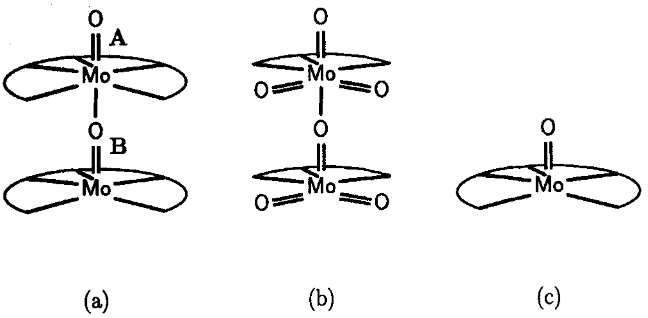
Molybdenum Complex

In a template synthesis starting from an ethanolic solution of $MoOCl_3$, dap, and sox (in the molar ratio 1 : 1 : 2) the $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ dimer was obtained. Its stoichiometry was confirmed by conductometry: the value of 497 Ω^{-1}cm^{2}mol^{-1} corresponds to six chloride ions in the outer coordination sphere. The presence of uncoordinated (lattice) water molecules was confirmed by thermal analysis. Lattice water was removed in a single endothermic step at 60°C.

The IR spectrum shows a single very intense band at 1690 cm^{-1} due to uncoordinated terminal carbonyl groups, suggesting that two adjacent chains of each H_2dapsox are coordinated in the same way to both Mo(V) atoms. There is also a single band at 1295 cm^{-1} due to ν(C—O) of the protonated α-oxyazine fragment (=N—N=C—OH), indicating the symmetrical coordination of the acylhydrazone through O donors.

In the case of symmetrical coordination H_2dapsox ligand acts as a quinquedentate [1–4] through pyridine, two azomethyne (imine) nitrogens, and two α-oxyazine oxygens. Such coordination is also postulated for the present dimeric structure. Due to the planarity of the chelate ligand systems the oxo substituents on Mo(V) are required to adopt a linear O═Mo—O═Mo configuration. The IR band at 915 cm^{-1} corresponds to the terminal Mo—O bond which is weakened in the presence of the oxygen bridge. This *trans* influence is obviously mutual since the bridged Mo—O bonds appear also to be weak on the basis of the 680 cm^{-1} vibration assigned to them. In the analogous porphyrin complex this band appears at 630 cm^{-1} [12]. Weakening of the oxo bridge is due to the *trans* configuration of both terminal oxygen atoms. In the region 250–500 cm^{-1} there are no bands for Mo—Cl bonds [13]. Therefore, the IR spectrum confirms the structure of the $[Mo_2O_2(H_2dapsox)_2]^{6+}$ cation as shown in Scheme 2(a).

Apart from the low-temperature dehydration, thermal analysis shows a marked exothermic decomposition which starts at 225°C, and proceeds in two steps. In the first step Cl_2, four HCl molecules, and four —N═C—C(═O)—NH_2 fragments are removed (the latter probably as NC—CO—NH_2 molecules), while the coordinated α-oxyazine O atoms remain bonded to metal atoms ($\Delta M_{obs} = 43.11\%$; $\Delta M_{calc.} = 42.30\%$). The cleavage of N—N instead of N—C bonds in the chains of coordinated H_2dapsox confirms the double-bonded nature of N—C and the presence of the α-oxazine form. In this step Mo(V) has been oxidized and transformed into an intermediate Mo(VI) complex shown in Scheme 2(b). It represents a rare example of an unstable trioxo complex (like MoO_3(triamine) [14], MoO_3(dien) [15], or $[MoO_3(edta)MoO_3]$ [16]), which is decomposed exothermically into MoO_3 in the second step ($\Delta M_{obs} = 27.29\%$; $\Delta M_{calc} = 27.06\%$). The IR spectrum of the intermediate compound shows bands at 835 and 878 cm^{-1} characteristic for the MoO_3 group [15], as well as a band at 662 cm^{-1} which is presumably due to the bridge.



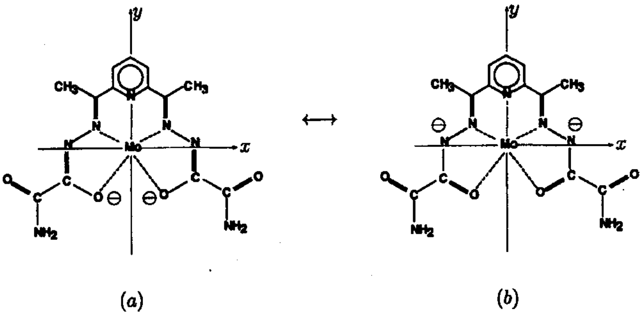
(a) (b) (c)

SCHEME 2

TG and DSC curves point to the stability of the dimeric structure in the solid state since there is no indication of polymerization or of Mo—O bond cleavage. However, in water the dimer undergoes dissociation which is evident from the bands in the electronic spectrum characteristic of the Mo(V) monomeric species [17]. In addition, the monomerization is accompanied by deprotonation of the H_2dapsox ligand as evidenced by a marked decrease in solution pH value (1.92 for a 0.05 molar solution of $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$). It is possible that the presence of two oxo atoms in *trans* positions together with short non-bonded distances between adjacent quinquedentate chelate ligands destabilizes the deprotonated forms of the acylhydrazone in the case of the dimeric structure [12].

In square pyramidal MoO^{3+} complexes with strong axial Mo—O interactions, the order of *d*-orbitals is $b_2(d_{xy}) < e(d_{xz}, d_{yz}) < b_1(d_{x^2-y^2}) < a_1(d_{z^2})$. The ground state of Mo(V) is $^2B_2$ (configuration d^1_{xy}) leading to three possible $d-d$ transitions to ^2E, $^2B_1$ and $^2A_1$, occurring at 600 nm, between 400–450 nm, and below 400 nm, respectively. The latter transition is masked by strong ligand-to-metal charge transfer bands [18]. In our case the monomeric complex, which is formed by dissolving $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ in water, is pentagonal pyramidal (Scheme 2(c)). The presence of five ligators in the chelate plane (instead of four) raises the energy of b_1 and b_2 orbitals when compared to the square pyramidal coordination. However, strong metal-ligand interactions with the axial oxo ligators dominate the Mo(V) ligand field leaving the overall order of orbital energies the same as in the square pyramidal coordination.

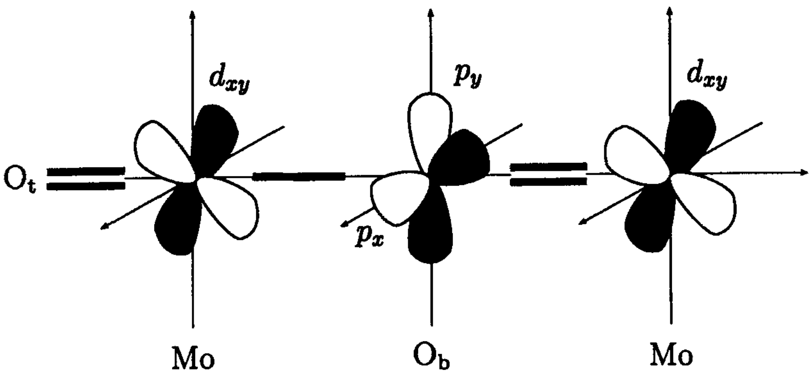
The electronic spectrum of $[MoO(dapsox)]^+$ shows three bands at 650 nm (with a shoulder at 698 nm), 490 nm and 410 nm, assigned to ^2E, $^2B_1$ and $^2A_1$ transitions, respectively. In comparison to the majority of Mo(V) monomeric species, all bands are shifted to higher wavelengths [6]. A possible cause for the weakening of the ligand field is the presence of two negatively charged oxygen atoms of the α-oxymazine fragments (Scheme 3(a)) which point towards the lobes of the d_{xy} orbital thus increasing its energy and decreasing the HOMO-LUMO separation. Furthermore, the presence of a shoulder for the $^2B_2 \rightarrow {}^2E$ transition indicates removal of degeneracy of the $e(d_{xz}, d_{yz})$ level. This may be due to the presence of two nitrogen atoms (negatively charged in one of the resonance structures of the ligand) pointing along the x-axis direction (Scheme 3(b)) and thus increasing the energy of the d_{xz} in comparison to the d_{yz} orbital. Intraligand transitions occur at 345 and 302 nm. They are also shifted towards higher wavelengths with respect to the free ligand (315 and 277 nm). All these results support the idea that the quinquedentate ligand in the $[MoO\ (dapsox)]^+$ monomer exists



SCHEME 3

in a stable deprotonated and electronically delocalized form. It is interesting to note that Chandhury [13, 19, 20] assigned the 650 nm transition in heptacoordinated Mo(V) complexes with carbodithiolates to a ligand-to-metal charge transfer transition, S → Mo. We believe that our 650 nm band is due to pentacoordination of the chelate system in the xy-plane, and that the spectra of carbodithiolate complexes might be reinterpreted in the same way.

The room-temperature magnetic moment of $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ dimer is 0.95 BM per Mo atom. The paramagnetism of this compound was expected due to the linearity of the O=Mo—O=Mo fragment. Namely, as in the case of $[Mo_2O_3(TPP)_2]$ with a linear O=Mo—O—Mo=O bridge, the singly occupied d_{xy} orbital of Mo cannot overlap with the oxygen $p\pi$ orbitals nor can it form a three-centered π bond involving Mo—O—Mo fragment (Scheme 4) that could lead to spin pairing and diamagnetism. However, in spite of the fact that both



SCHEME 4

$[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ and $[Mo_2O_3(TPP)_2]$ are possibly unique examples of μ-oxo dimolybdenum(V) structures with *trans* disposition of the Mo—O (terminal) and Mo—O (bridged) bonds, their magnetochemistry is different. In our structure one of the formally terminal oxo atoms acts also as a bridging atom so that either d_{xz} or d_{yz} orbital on the pentagonal pyramidal Mo atom remains nonbonded. Due to pentacoordination in the ligand xy-plane, the singly occupied d_{xy} orbital is no longer nonbonded, as in $[Mo_2O_3(TPP)_2]$, but together with $d_{x^2-y^2}$ it engages in bonding with the planar acylhydrazone ligator atoms. In case of $[Mo_2O_3(TPP)_2]$ each unpaired electron is localized in a d_{xy} orbital on the corresponding Mo(V) atom [21]. Although the Mo···Mo distance in the TPP complex is not large, as for example in the $[Mo(V)]_2$-glutathione complex [22], the coupling between Mo(V) centers is almost negligible, and exchange splitting (separation between singlet and triplet spin state) remains large [21], with a magnetic moment of 1.7 BM per Mo(V) [7]. However, unlike the TPP complex, in $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ bonds between Mo(V) and quinquedentate ligator atoms have an increased covalent character so that the *d* electron on both Mo(V) atoms is to a greater extent engaged in delocalization on the chelate ligand by the in-plane $d\pi$ back donation mechanism, and the consequence is the mentioned magnetic moment of 0.95 BM per Mo(V) atom.

A similar interaction was proposed for the $[Fe(H_2O)(dapoamh)]_2O$ dimer[1] in which case it leads to overall diamagnetism [23]. In the iron(III) dimer the planar chelate ligand is doubly deprotonated and fully conjugated, thus increasing the extent of electron delocalization in the xy-plane.

Similar to the Fe(III) binuclear complex the monomeric pentagonal pyramidal species $[MoO(dapsox)]^+$, formed by dissolving $[Mo_2O_2(H_2dapsox)_2]Cl_6 \cdot 4H_2O$ in water, has a doubly deprotonated quinquedentate acylhydrazone (Scheme 3). The magnetic moment measured in solution (1.82 BM) indicates the presence of one unpaired electron in $[MoO(dapsox)]^+$. Solution EPR spectra at room temperature reveal only one isotropic signal ($g = 1.981$) accompanied by six satellites due to the hyperfine coupling with $^{95,97}Mo$ nuclei. In addition, the 77 K EPR spectrum shows axial symmetry with $g_{\parallel} = 2.110$ and $g_{\perp} = 1.917$. These spectra are typical for Mo(V) monomeric species.

A larger $g_{\parallel}$ value in comparison to the majority of the other monomeric Mo(V) species [6, 24] points to greater covalent character of this monomeric structure and a low charge transfer excitation energy. Transitions from low

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[1] $H_2dapoamh$ is obtained from $H_2dapsox$ by hydrolysis of amide groups.

lying filled ligand orbitals to the b_2 (d_{xy}) orbital on the metal cause a large positive shift of $g_{\parallel}$ values [25]. The decrease of charge transfer excitation energy is a consequence of extended delocalization of the doubly deprotonated ligand along the entire chain. In addition, in the pentagonal pyramidal structure of $[MoO(dapsox)]^+$, the d_{xz} orbital becomes available for π bonding with the corresponding orbitals on the ligator atoms of the planar acylhydrazone. It was already mentioned that electronic spectrum provides evidence for the increase in energy of the d_{xz} orbital due to the interaction with the filled orbitals of hydrazide nitrogen ligators pointing along the x-axis (Scheme 3). The line widths and large hyperfine coupling constants in the EPR spectra of both dimeric and monomeric species is also noteworthy.

Kikuchi and coworkers [24] classified Mo enzymes and monomeric Mo(V) complexes into two types on the basis of their EPR parameters ($g_{\parallel}$ and $g_{\parallel} - g_{\perp}$). Type one was assigned to octahedral and type two to square pyramidal structures. Type one is characterized by greater g anisotropy (larger $g_{\parallel} - g_{\perp}$), greater delocalization, and a greater extent of overlap between Mo orbitals and π ligator orbitals in the xy-plane. On the basis of the criteria in Ref. [24] ($f(g_{\parallel}) = g_{\parallel} - g_{\perp}$), our $[MoO(dapsox)]^+$ cation exhibits more pronounced difference in $g_{\parallel}$ and $g_{\perp}$ values, and a larger $g_{\parallel}$ value than both square pyramidal and octahedral complexes [24], so it is best described as a new (third) type of structure. Due to the presence of five ligators in a chelate plane, properties of the present structure are more strongly affected by the electron delocalization than in types one and two [24]. Due to the lack of other examples of pentagonal pyramidal Mo(V) complexes it remains to be seen whether such systems could be characterized by similar EPR properties and constitute a new type of Mo(V) complex.

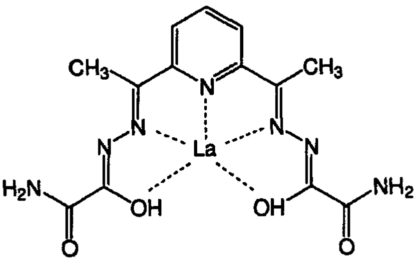
Lanthanum Complex

In a template synthesis from ethanolic solution of $La(NO_3)_3 \cdot 6H_2O$, dap, and sox (in the molar ratio 1 : 1.2) a monomeric La(III) complex was obtained. On the basis of elemental and thermal analyses, as well as IR spectra, the composition of this compound is $[La(H_2dapsox)(NO_3)_x](NO_3)_{3-x} \cdot EtOH$, ($x = 1, 2$). Thermal analysis shows the presence of the uncoordinated (lattice) ethanol molecule (1 mol EtOH per 2 mol of complex). Removal of lattice EtOH starts at 50°C and the desolvated structure is stable to 230°C, when it starts to decompose in two exothermic steps. The first is characterized by the removal of $H_2N{-}C({=}O){-}C({=}O){-}NH{-}$ fragment (23.71%). After the second step only La_2O_3 remains. Thermal analyses of Co(II), Cu(II), Ni(II), Fe(III), MoO^{3+} and U_2O^{2+} complexes with H_2dapsox ligand [2, 5], and its singly or doubly deprotonated forms revealed that whenever the side chains carry equal charges and have symmetric pentacoordination through N (from pyridine and two azomethyne groups) and O (from two hydrazide groups), decomposition of the multidentate starts with cleavage of N—N bonds and proceed symmetrically in two steps. The cleavage of N—N instead of N—C bonds confirms the double-bonded nature of N—C bond and the presence of α-oxyazine form.

IR spectra of the complex show bands characteristic of a symmetrical pentacoordination of H_2dapsox in the neutral form [4]. On the basis of the results of thermal analyses and IR spectra, the coordination of H_2dapsox to the La(III) ion is presented in Scheme 5. The IR spectrum of the La(III) complex shows bands at $1358\,cm^{-1}$, $1304\,cm^{-1}$ and $1041\,cm^{-1}$, characteristic of bidentate coordination of NO_3^-, while bands at $1385\,cm^{-1}$ and $822\,cm^{-1}$ represent uncoordinated NO_3^- in the outer coordination sphere. There is also one band at $493\,cm^{-1}$ due to ν(La—O) vibration [26].

Molar conductivity in DMSO was $133.7\,\Omega^{-1}cm^2mol^{-1}$, which confirms the coordination of one NO_3^- group. However, it is possible that the second NO_3^- group undergoes dissociation in DMSO, leaving the possibility for one or two DMSO molecules to be coordinated. In the solid state it is likely that both NO_3^- groups are coordinated. In that case the coordination number of lanthanum is 9, with equatorially coordinated quinquedentate, and axially coordinated NO_3^- ions as bidentates. Hydrogen bonds between the quinquedentate and one of the coordinated NO_3^- groups prevent the dissociation of the latter and contribute to the stability of the $[La(H_2dapsox)(NO_3)S_x]^{2+}$ cation (where S is a unidentate solvent molecule, and $x = 1$ or 2).

Lanthanum complexes with similar multidentate ligands usually have coordination numbers from 8–12. Thus with 2,6-diacetylpyridine bis(semicarbazone), (dapsc), $[La(dapsc)(H_2O)_4](ClO_4)_3$ with coordination number 9



SCHEME 5

was obtained [27]. A reaction with a macrocyclic sexidentate ligand (L) (prepared by the condensation of 2 moles of dap and 2 moles of ethylenediamine) yielded two complexes, one with coordination number 12, $[La(L)(NO_3)_3]$ [28], and the other with hexagonal bipyramidal geometry, $[La(L)(H_2O)_2](ClO_4)_3$ [29]. A similar samarium complex, $[Sm(L')(NO_3)(OH)(H_2O)]NO_3 \cdot 2MeOH$, was obtained with a macrocyclic sexidentate (L′) formed by condensation of pyridinecarbaldehyde and ethylenediamine [30]. As in our case the samarium complex possessed both coordinated and uncoordinated NO_3^- groups. There was also an axially coordinated water molecule, an OH^- ligand on one side (instead of the second NO_3^- group) and NO_3^- on the other side of the equatorial sexidentate. In this case one molecule of water coordinated Sm^{3+} ion with its much smaller radius, and was deprotonated as a result of the increased effective nuclear charge of the central metal atom.

Preparation of the $[La(dapbah)(NO_3)_3]$ complex (dapbah = 2,6-diacetylpyridine-bis(benzoatohydrazone)), with coordination number 11 was also described [31]. Structures with coordination number 11 are very rare because they easily transform into structures with coordination number 12, which have smaller repulsive interactions. It was also unusual that the complex does not contain any molecule of solvent in the coordination sphere or in the lattice. In fact, La^{3+} is a hard acid and usually highly hydrolyzed. The absence of solvent in this structure was explained by the presence of large hydrophobic phenyl groups which imposed specific packing of the molecules.

In contrast to the analogous complexes obtained from $La(NO_3)_3$, our La(III) complex in the solid state possesses only two coordinated NO_3^- groups [28, 31]. We assume that this is a consequence of nonbonding interactions, because a third NO_3^- group would increase repulsive interactions with uncoordinated carbonyl groups of H_2dapsox.

In structures mentioned above [28, 31] with three NO_3^- groups in the coordination sphere, the multidentate ligand did not contain uncoordinated oxygen atoms; thus the repulsive interactions between the multidentate and NO_3^- groups were weaker. It is possible that nonbonding interactions impose the absence of solvent molecules in the coordination sphere in the solid state, and prevent the coordination of more than two unidentate solvent molecules in the solution. However, the complex $[La(dapsc)(H_2O)_4](ClO_4)_3$ was obtained [27] from $La(ClO_4)_3$, and has two coordinated water molecules above and below the quinquedentate plane. The existence of coordination number 9 in that case offers support for our proposed structure of the present La(III) complex.

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