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Synthesis of a New Binucleating Ligand and Its Interaction with Dioxouranium(VI) and Copper(II)

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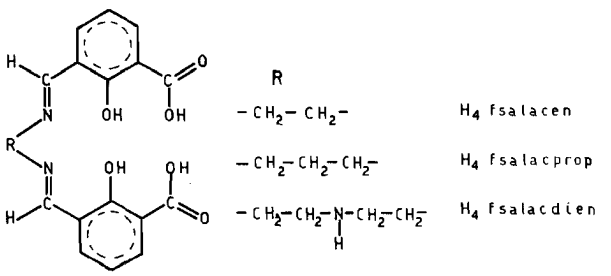
In the course of our studies on the coordination chemistry of uranyl(VI) ion, we have been interested in the preparation of binuclear complexes in relation to the interaction between a hard and a soft metal ion.[1-5] In this paper we report the synthesis and characterization of new binucleating ligands derived from 3-formylsalicylic acid and diamine and their mononuclear and binuclear complexes:



The 3-formylsalicylic acid (H_2fsalac) was prepared according to literature methods;[6] its purity was checked by microanalytical data and melting point. From the reaction of 3-formylsalicylic acid with the appropriate diamine only the ligand H_4fsalacen was isolated in the solid state; the other ligands have been obtained by template synthesis.

The copper(II) complexes were prepared from the reaction of stoichiometric amount of 3-formylsalicylic acid, diamine and copper(II) acetate in methanol according to the scheme:

$$\begin{array}{l} \qquad\qquad [CuH_2\text{fsalac(diam)}]\,xH_2O\ (x = 0,1,2) \\ \qquad\qquad\qquad\quad \text{en} \\ \qquad\qquad\qquad\quad \text{dien} \\ Cu(CH_3COO)_2 4H_2O + 2H_2\text{fsalac} \\ \qquad\qquad\qquad\quad 1,3\text{-prop} \\ \qquad\qquad\qquad\quad [Cu_2\text{fsalac(prop)}]\,H_2O \end{array}$$

Analytical data are in accordance with the proposed formulation; the compounds require molecules of water in their formulation as shown by their analytical data and i.r. spectra.

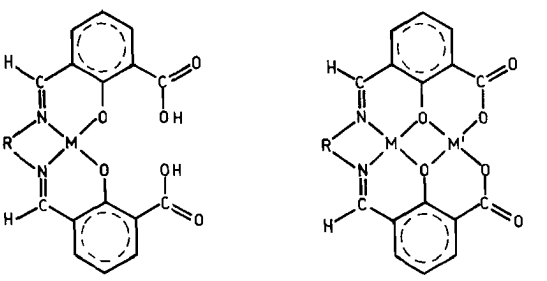
The i.r. spectra of these complexes are reported in the table; the spectra of both types of complexes are characterized by the absence of bands due to free or coordinated $-NH_2$ group, suggesting the presence of a completely condensed Schiff base ligand. Furthermore, the mononuclear compounds show bands attributable to the vibration $\nu C{=}O$ of a free carboxylic group at about 1700 cm^{-1}. Attempts to prepare the mononuclear uranyl(VI) complex from the 3-formylsalicylic acid and ethylenediamine under a variety of conditions yielded products of unknown composition; well defined complexes were obtained only through the following reactions:

$$UO_2(NO_3)_2 \cdot 6H_2O + 2H_2\text{fsalac} + 4LiOH \xrightarrow{\text{EtOH}} Li_2[UO_2(\text{fsalac})_2(H_2O)_2] + 2LiNO_3 + 8H_2O \quad (1)$$

$$Li_2[UO_2(\text{fsalac})_2(H_2O)2] + \text{en} \xrightarrow{\text{EtOH}} Li_2[UO_2\text{-(fsalac(en))}H_2O] + H_2O \quad (2)$$

en = ethylenediamine; H_2fsalac = 3-formylsalicylic acid

It is reasonable to suppose that the coordination around the uranyl ion occurs through the carboxylic oxygen and the two phenolic oxygen atoms. The i.r. spectrum in the 1700–1300 cm^{-1} region supports this formulation: the bands at 1652 and 1600 cm^{-1} may be assigned to the $\nu C{=}N$ and $\nu C{=}O$ vibrations respectively while the band at 1310 is assigned to C–O of the phenolic group. The mononuclear CuH_2-fsalacen readily forms binuclear complexes when treated with nickel(II), thorium(IV), and uranyl(VI) acetates. Their proposed configuration is the following:



M = Cu^{2+}, Ni^{2+}; M' = Cu^{2+}, Ni^{2+}, UO_2^{2+}, $Th^{4+}/_2$

A broad band at 3400 cm^{-1} in their i.r. spectra is assigned to the asymmetric stretching vibration of the H_2O molecules found in the complexes.

TABLE. Some Significant Infrared Frequencies of the Prepared Complexes.

Compound	$\nu_{C=N}$	$\nu_{C=O}$	Other Bands
H_2fsalac	–	1675	3543 ν_{OH}
H_4fsalac(en)	1652	1700	3430 ν_{OH}
[H_2fsalac(en)Cu]	1642	1705	
[H_2fsalac(dien)Cu]	1645	1695	3220 ν_{N-H}
[fsalac(prop)Cu_2]	1640	1595	
[fsalac(en)Cu Ni] H_2O	1640	1610	3420 ν_{OH}
[fsalac(en)Cu UO_2]	1650	1595	919 ν_3O—U—O, 260 ν_2O—U—O
[(fsalac(en)Cu)$_2$Th] $(H_2O)_2$	1640	1598	3460 ν_{OH}
Li_2[(fsalac)$_2UO_2(H_2O)_2$]	–	1600	3400 ν_{OH}, 1680 $\nu_{-CH=O}$, 920 ν_3O—U—O, 260 ν_2O—U—O
Li_2[fsalac(en)UO_2H_2O]	1650	1600	3400 ν_{OH}, 900 ν_3O—U—O, 268 ν_2O—U—O

As above the bands near 1650 and 1600 cm^{-1} may be attributed to the stretching modes of the C=N azomethynic and C=O carboxylato groups.

Furthermore, it is also possible to prepare a series of binuclear complexes with the same or different metal ions; this investigation is now in progress.

References

1 U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Nucl. Chem. Letters, 10,* 437 (1974).
2 M. Vidali, P. A. Vigato, U. Casellato, E. Tondello and O. Traverso, *J. Inorg. Nucl. Chem., 37,* 1715 (1975).
3 P. A. Vigato, M. Vidali, U. Casellato, R. Graziani and F. Benetollo, *Inorg. Nucl. Chem. Letters, 11,* 597 (1975).
4 M. Vidali, U. Casellato, P. A. Vigato and R. Graziani, *J. Inorg. Nucl. Chem.*, in press.
5 R. Graziani, U. Casellato, M. Vidali, and P. A. Vigato, *Acta Cryst.*, in press.
6 J. C. Duff and E. J. Bills, *J. Chem. Soc.*, 1978 (1932).