# Novel Schiff Base Complexes of some f-Transition and Related Elements*

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Since the successful synthesis of 2,5-pyrroledicarboxaldehyde we have been investigating transition metal complexes of Schiff bases derived from this dialdehyde. Thus, the reactions of 2,5-pyrrolediylbis[*N*-(*o*-hydroxyphenylaldimine)] ($SBH_2$) with d-transition elements have been investigated [1]. The behaviour of $SBH_2$ has been shown to be almost identical to the behaviour of the corresponding Schiff base derived from 2,6-pyridinedicarboxaldehyde. We were interested in finding out if such a similarity existed in the case of f-transition elements. The reactions of 2,6-pyridinediylbis[*N*-(*o*-hydroxyphenylaldimine)] with f-transition metal ions have already been reported [2]. We hereby report on the corresponding reactions of $SBH_2$.

## Experimental

2,5-Pyrroledicarboxaldehyde was synthesized from pyrrole by step-wise introduction of the aldehyde groups in the 2 and 5 positions [3]. It was then condensed with freshly purified *o*-aminophenol in hot water [1]. The yellow Schiff base thus obtained ($SBH_2$) was recrystallized from hot benzene; m.p. 184–185 °C.

Nitrate hydrates of Sc(III), Y(III), La(III), Gd(III), Er(III), Dy(III) and Pr(III) were prepared from the corresponding oxides by dissolution in nitric acid followed by evaporation to dryness, and heating in an oven to 100 °C.

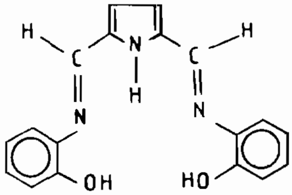
Schiff base complexes were prepared by reacting equimolar amounts of $SBH_2$ and the metal salt in refluxing methanol for 1 h. The product was washed with methanol and ether, respectively, and dried. The nitrate hydrates of Sc(III), Y(III), La(III), Gd(III), Er(III), Dy(III), Pr(III), Ce(IV) and Th(IV) and $UO_2(CH_3COO)_2$ were thus reacted.

## Results

All the ions studied afforded 1:1 complexes of the Schiff base $SBH_2$. Thus, the complexes $M(SBH)(NO_3)_2 \cdot nH_2O$ were obtained where $n = 1$, M = Gd(III), Er(III), Dy(III) and Pr(III); and $n = 2$, M = Sc(III), Y(III) and La(III). These complexes showed electric conductance in nitrobenzene corresponding to three moles of ions per mole of the dissolved complex. The IR spectra showed strong $\nu$(NH) bands at 3300 $cm^{-1}$ and $\nu$(C=N) around 1600 $cm^{-1}$. A broad absorption at 3400 $cm^{-1}$ indicates a strongly hydrogen-bonded hydroxyl group.

Thorium(IV) and $UO_2^{2+}$ afforded $Th(SB)(NO_3)_2 \cdot H_2O$ and $UO_2(SB)$, respectively; Ce(IV) gave $Ce(SBH)(NO_3)_3(H_2O)_2$. All complexes gave C, H and N analyses consistent with the proposed molecular formulae. They all melt with decomposition between 230 and 340 °C. They are all orange to red in color, insoluble in most common solvents, but soluble to some extent in DMF, DMSO and nitrobenzene.

The Schiff base $SBH_2$ (I) is potentially tetradentate because of the two azomethine nitrogens and the two phenolate oxygens. We have previously shown [4] that the pyrrole nitrogen is not involved in bonding to the metal unless the complexation reaction is carried out in a medium basic enough to effect the deprotonation of the pyrrole nitrogen. We have also shown that $SBH_2$ reacts as $SB^{2-}$ with d-transition metal ions [1].



$SBH_2$ (I)

$SBH_2$ does indeed retain the pyrrole N–H bond in its reaction with all the ions studied in the present work, as evidenced by the strong $\nu$(NH) band at 3300 $cm^{-1}$. However, it behaves as $SB^{2-}$ only in its reactions with Th(IV) and $UO_2$(II). With all other ions it behaves as $SBH^-$. Apparently short hydrogen bonding similar to that occurring in dimethylglyoximate complexes is encountered. Strong hydrogen bonding is evidenced by the broadening of the band at 3400 $cm^{-1}$ and the occurrence of a weak band at 850 $cm^{-1}$. This is observed only when the Schiff base reacts as $SBH^-$. This suggests that in these complexes, each Schiff base ligand retains one phenolic hydrogen which is held with an equal strength by the two phenolate oxygens. These phenolate oxygens are, in their turn, bonded to the metal atom (II).

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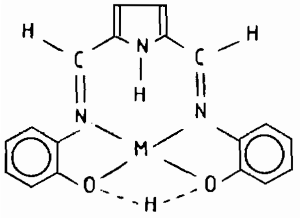

M(SBH)$^{2+}$ (**II**)

The nitrate ligands are known to be very weak ligands. They are almost totally ionically bonded to the metal. This explains the observed conductance of the solutions of the complexes in which they behave as 1:2 electrolytes. The Ce(IV) complex behaves as a 1:3 electrolyte; $UO_2(SB)$ is a non-electrolyte. With $SBH^-$ bonded as a tetradentate ligand (**II**), the minimum coordination number of the complexes is six. However, the water molecules appearing in the molecular formulae of the complexes could very well be incorporated in the coordination sphere rather than being molecules of hydration. This is consistent with the high coordination number commonly encountered with f-transition metal complexes.

In conclusion, the behaviour of $SBH_2$ with f-transition elements is almost identical with the behaviour of the 2,6-pyridine Schiff base. This once more confirms the non-involvement of the pyrrole or the pyridine nitrogens in bonding to the metal.

## References

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