

Synthesis and Properties of Some Transition Metal Complexes of Schiff Base Derived from the Condensation of 2,6-Pyridinedicarboxaldehyde and 8-Aminoquinoline

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The Schiff base derived from the condensation of 8-aminoquinoline and 2,6-pyridinedicarboxaldehyde has been synthesized by two routes. Direct reaction of the amine and the dialdehyde lead to the formation of the Schiff base which was then used to synthesize a number of transition metal-schiff-base complexes. In another procedure metal salts were reacted with a mixture of the amine and the dialdehyde to yield schiff-base-metal complexes. The decomposition of one of these complexes yielded the required Schiff base. Complexes synthesized by either route were isolated and mono-, di- and trinuclear species were identified.

Key Words: 2,6-Pyridinedicarboxaldehyde, Transition metals, 8-Aminoquinoline, Schiff base, Complexes.

INTRODUCTION

The reactions of schiff bases derived from the condensation of 2,6-pyridinedicarboxaldehyde (DIAL) and *o*-aminobenzene-thiol with several transition metal ions have been investigated^{1,2}. These Schiff bases have been shown to react in various ways; one of them being the expected behaviour of the Schiff base as an anion or dianion. The condensation of diaminopyridine with DIAL yields polymeric species³. We now report the synthesis of the Schiff base derived from DIAL and 8-aminoquinoline and its transition metal complexes. Complexes of such a Schiff base find significant applications in catalysis, analytical chemistry and bioinorganic chemistry⁴⁻⁶.

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EXPERIMENTAL

Synthesis of the Schiff base (SB)

A hot solution of 2,6-pyridinedicarboxaldehyde (DIAL)⁷ (3 mmol) in 30 mL water was added to a hot solution of 8-aminoquinoline (6 mmols) in 450 mL water. The reaction mixture was refluxed for 0.5 h then allowed to cool down at room temperature. Sodium chloride was added to salt out a pale yellow product that was filtered off, washed thoroughly with cold water, and dried in vacuum over P₂O₅ at 50°C. Yield: 1.0 g, 86% The product is soluble in benzene, acetone, toluene and hot ethanol; insoluble in water and ether. M.p.: 210-215°C. Analysis: Calcd. for C₂₅H₁₄N₅: C 77.50, H 4.42, N 18.08. Found: C 77.31, H 4.85, N 18.53. Another form of the product was prepared which gave the analysis: Calcd for C₂₅H₁₇N₅.H₂O: C 74.05, H 4.72, N 17.28. Found: C 73.83, H 4.75, N 17.94.

Reaction of the Schiff base (SB) with metal ions:

Pd(C₆H₅CN)₂Cl₂: A solution of Schiff base (0.132 g, 0.33 mmol) in benzene (3 mL) was added to a filtered solution of Pd(C₆H₅CN)₂Cl₂ (0.192 g, 0.50 mmol) in benzene (7 mL). The mustard precipitate was immediately formed was filtered off, washed with benzene, then with ether and dried in vacuum over P₂O₅ at 50°C. The product decomposes at 250°C and is insoluble in common organic solvents and water, but soluble in DMF and DMSO.

CuCl₂.2H₂O: A solution of the Schiff base (0.132 g, 0.33 mmol) in acetone (2 mL). The mixture was stirred at room temperature for 0.5 h. The green solid that separated was filtered off, washed with acetone, then with ether and dried in vacuum over P₂O₅ at 50°C. The product melts with decomposition at 194-196°C. It is slightly soluble in methanol and water, soluble in DMF and DMSO and insoluble in benzene, chloroform and acetone.

K₂PtCl₄: A filtered aqueous solution of 0.208 g. (0.50 mmol) of K₂PtCl₄ in 3 mL water was added to a solution of 0.132 g (0.33 mmol) of Schiff base in 3 mL acetone. A green precipitate separated immediately. The mixture was stirred at room temperature for 2 h. The precipitate was then filtered off, washed with water, acetone and ether, respectively, and dried in vacuum over P₂O₅ at 50°C. The product melts with decomposition at 290°C. It dissolves in DMF and DMSO, but insoluble in benzene, ether, acetone, methanol or water.

RhCl₃.3H₂O: A hot solution of the schiff base (0.132 g, 0.33 mmol) in ethanol (15 mL) was added to a solution of 0.13 g (0.5 mmol) of RhCl₃.3H₂O in ethanol. A mustard solid was formed. It was filtered off and washed with hot ethanol and finally then with ether. It was then dried in vacuum over P₂O₅ at 50°C. The product decomposes at 305°C. It is soluble in DMSO but

insoluble in benzene, ether, acetone, chloroform, methanol, ethanol and water.

Other transition metal salts: A procedure similar to that used for $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was applied to the reaction of the Schiff base with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, ZnCl_2 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, HgCl_2 , HgBr_2 , $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, CuBr_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. All these salts afforded products that were soluble in DMF and DMSO and insoluble in other common organic solvents and water.

The colours, melting points (with decomposition) and elemental analyses of the Schiff base complexes are listed in Table-1.

TABLE-1
COLOUR, M.P. ANALYTICAL DATA OF TRANSITION METAL COMPLEXES OF SCHIFF BASE (REACTION OF SCHIFF BASE WITH METAL IONS)

Compound	m.p. (°C)	Colour	(% Analysis (Calcd) Found)		
			C	H	N
$\text{Co}(\text{SB})(\text{ClO}_4)_2$	290	Light brown	(46.53) 46.61	(2.66) 2.96	(10.85) 10.48
$\text{Fe}(\text{SB})(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	190	Dark green	(45.48) 45.80	(2.90) 3.14	(10.61) 10.03
$\text{Fe}_2(\text{SB})\text{Cl}_6$	235-240	Light brown	(42.18) 41.76	(2.41) 2.34	(9.84) 9.64
$\text{Zn}_2(\text{SB})\text{Cl}_4$	250	Yellow	(45.49) 46.32	(2.60) 2.49	(10.61) 10.54
$\text{Cu}_2(\text{SB})\text{Cl}_4 \cdot 2\text{H}_2\text{O}$	194-196	Green	(43.36) 43.77	(3.06) 2.92	(10.12) 10.20
$\text{Cu}_2(\text{SB})\text{Br}_4 \cdot \text{H}_2\text{O}$	205-210	Green	(35.21) 34.65	(2.25) 2.24	(8.21) 8.17
$\text{Rh}_3(\text{SB})_2\text{Cl}_9 \cdot 3\text{H}_2\text{O}$	305	Mustard	(41.22) 41.38	(2.77) 2.87	(9.62) 9.26
$\text{Ru}_2(\text{SB})\text{Cl}_6 \cdot \text{H}_2\text{O}$	330	Green-black	(36.60) 37.14	(2.33) 2.32	(8.54) 8.69
$\text{Pt}(\text{SB})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	290	Green	(55.76) 56.03	(3.56) 3.74	(13.01) 13.25
$\text{Hg}_2(\text{SB})\text{Cl}_4$	210-216	Yellow	(32.27) 32.98	(1.84) 1.83	(7.53) 7.60
$\text{Hg}_2(\text{SB})\text{Br}_4$	208-210	Yellow	(27.09) 27.22	(1.55) 1.49	(6.32) 6.32
$\text{Pd}(\text{SB})\text{Cl}_2 \cdot \text{H}_2\text{O}$	250	Mustard	(51.53) 50.81	(3.29) 3.49	(12.02) 11.75

Reactions of a mixture of 8-aminoquinoline and 2,6-pyridinedicarboxaldehyde with metal salts

The reactions of a mixture of 8-aminoquinoline and DIAL were carried out in an attempt to effect their condensation in the presence of metal ions to form metal-schiff-base complexes directly. Two general procedures were followed:

(i) To a stirred hot solution of 8-aminoquinoline (0.288 g, 2 mmols) in acetone (20 mL), DIAL (0.135 g, 1 mmol) was added, followed directly by the addition of a solution of the metal salt (1 mmol) in the appropriate

solvent (10-15 mL). Acetone was used for Cu(II) and Co(II) salts, and ethanol for Ag(I), Rh(III), Ru(III) and Zn(II) salts. The reaction mixture was refluxed for 1-3 h. The product was filtered off and washed with the reaction solvent and dried in vacuum. This procedure was used for the reactions of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, AgClO_4 , $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and ZnCl_2 .

(ii) To a stirred hot solution of the metal salt (0.74 mmol) in ethanol (10-20 mL), DIAL (100 mg, 0.74 mmol) was added followed by 8-aminoquinoline (0.213 g, 1.48 mmol). The mixture was refluxed with stirring for 0.5 h. The product formed was filtered off, washed with ethanol and dried in vacuum. This procedure was followed in the reactions of CuBr_2 , $\text{Cd}(\text{NO}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ and HgCl_2 .

The reaction of K_2PtCl_4 with a mixture of DIAL and 8-aminoquinoline was carried out at room temperature with water as solvent of K_2PtCl_4 and ethanol for DIAL. The reaction time was 2 h. The colours and melting points (all with decomposition), and elemental analyses for the products obtained by the reaction of transition metal ions with a mixture of DIAL and 8-aminoquinoline are listed in Table-2.

TABLE-2
COLOUR, M.P. AND ANALYTICAL DATA OF TRANSITION METAL
COMPLEXES OF SCHIFF BASE (REACTION OF A MIXTURE OF
8-AMINOQUINOLINE AND 2,6-PYRIDINEDICARBOXALDEHYDE
WITH METAL IONS)

Compound	m.p. °C	Colour	(% Analysis (Calcd.) Found)			
			C	H	N	Cl
$\text{Co}(\text{SB})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	265-270	Brown	(44.06)	(3.10)	(10.28)	(10.41)
			43.69	2.87	10.11	10.06
$\text{Cu}(\text{SB})(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$	210-215	Greyish brown	(41.59)	(3.49)	(9.70)	(9.82)
			41.71	3.28	10.05	9.75
$\text{Cu}_3(\text{SB})_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$	194-195	Green	(46.68)	(3.60)	(10.89)	(16.54)
			45.94	3.38	10.15	16.80
$\text{Cu}_3(\text{SB})_2\text{Br}_6 \cdot 2\text{H}_2\text{O}$	210-215	Green	(40.55)	(2.59)	(9.46)	–
			40.72	2.46	8.91	–
$\text{Zn}_3(\text{SB})_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$	255-259	Yellow	(46.48)	(3.59)	(10.84)	(16.47)
			45.89	3.37	10.23	17.24
$\text{Ru}_3(\text{SB})_2\text{Cl}_9 \cdot 6\text{H}_2\text{O}$	330-335	Black	(39.89)	(3.08)	(9.30)	(21.20)
			40.55	3.33	9.00	20.24
$\text{Pd}(\text{SB})\text{Cl}_2 \cdot \text{H}_2\text{O}$	200-205	Mustard	(51.53)	(3.29)	(12.02)	–
			50.61	3.41	11.56	–
$\text{Cd}(\text{SB})(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	275-278	Yellow	(46.78)	(2.98)	(15.28)	–
			46.62	2.74	15.02	–
$\text{Rh}_3(\text{SB})_2\text{Cl}_9 \cdot 8\text{H}_2\text{O}$	290-295	Mustard	(38.83)	(3.26)	(9.06)	(20.72)
			38.67	3.56	9.21	19.93
$\text{Pt}_2(\text{SB})\text{Cl}_4 \cdot 2\text{H}_2\text{O}$	220-225	Green	(31.42)	(2.22)	(7.33)	–
			30.68	2.06	6.90	–

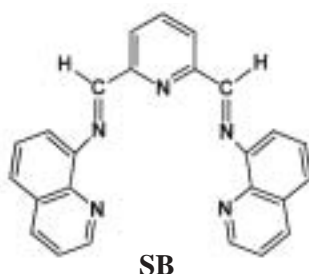
Decomposition of Pd(SB)Cl₂.2H₂O with KCN

The product obtained from the reaction of Pd(C₆H₅CN)₂Cl₂ with a mixture of DIAL and 8-aminoquinoline was decomposed by refluxing with aqueous solution (35%) of KCN for 0.5 h. After cooling, the mixture was extracted twice with chloroform. The extract was dried over anhydrous MgSO₄ and evaporated to dryness. The solid thus obtained was purified by dissolution in chloroform and precipitation with petroleum ether. The yellow product (SB) melted at 205-210°C with decomposition. It is soluble in chloroform and dioxane but insoluble in ether, water, ethanol and methanol.

The schiff base recovered was further reacted with Co(ClO₄)₂.6H₂O and Cd(NO₃)₂.4H₂O. The two products obtained were identical with those obtained from the respective reactions of Co(ClO₄)₂.6H₂O and Cd(NO₃)₂.4H₂O with a mixture of DIAL and 8-aminoquinoline.

RESULTS AND DISCUSSION

The condensation of 8-aminoquinoline with DIAL is expected to afford a neutral multidentate ligand with all-nitrogen donor atoms. The most favourable configuration will be square planar geometry in which the two 8-aminoquinoline groups are condensed with the aldehyde oxygens to occupy a syn-syn geometry with respect to the pyridine nitrogen of SB.



Other configurations may be encountered during the process of condensation because of the possible rotation about the ring-NH₂ bond in the 8-aminoquinoline and around the aldehyde (C=O) bond which may be reduced in bond order to about 1.0 during one or more of the steps of alodal condensation (addition-elimination). The formation of Schiff base with its favourable configuration will afford a versatile ligand that would make possible the synthesis of catalytically and biologically important coordination compounds.

The synthesis of the Schiff base has been attempted in the present work by two procedures: (a) direct reaction of 8-aminoquinoline and DIAL (b) *In situ* formation of Schiff-base-metal complexes by the reaction of a mixture of DIAL and 8-aminoquinoline with the metal salt. Upon

decomposition of Schiff-base-metal coordination compounds, the Schiff base may be recovered.

Thus, two sets of Schiff base-metal coordination compounds have been synthesized in the present work. The Schiff-base itself was prepared by the condensation of DIAL with 8-aminoquinoline. It is yellow solid melting at 210-215°C with decomposition. Its elemental analysis is consistent with the formula SB.H₂O. The schiff base was also prepared by the decomposition of Pd(SB)Cl₂.H₂O with aqueous KCN, followed by the extraction of the organic product. Upon evaporation and purification a yellow product identical to the above-mentioned schiff base was obtained.

Neither the Schiff base nor its compounds show any absorption in the ν(NH) range (3440-3340 cm⁻¹), indicating complete condensation of the aldehyde and the amine. The schiff base coordination compounds synthesized in this work are mono-, di- or trinuclear.

(a) Mononuclear compounds of the formula M(SB)X₂.mH₂O where

M = Co(II), X = ClO₄⁻, m = 0 or 2

M = Cd(II), X = NO₃⁻, m = 1

M = Cu(II) or Fe(II), X = ClO₄⁻, m = 4 or 1, respectively

M = Pd(II), X = Cl⁻, m = 1

In most of the compounds the anion is the perchlorate except for Pt(II) and Pd(II) where it is the chloride and Cd(II) where it is the nitrate. Both the perchlorate and nitrate ions are weak-field ligands and are present outside the coordination sphere. The metal ions involved in this class of compounds are either those with tendency to form square planar, tetra-coordinate complex, [Pt(II), Pd(II), Cu(II)], or may accept such configuration if they are forced into it. Water molecules do not necessarily occupy a coordination site in the complex. They may be associated with the anion, particularly the perchlorate or the nitrate.

The above considerations justify that the Schiff base (SB) utilizes at least four of its nitrogen atoms, preferably the aminoquinoline ones (for steric considerations) to form a square plane around the metal.

(b) Binuclear compounds of the form M₂(SB)X₄.mH₂O where

M = Zn(II), Hg(II), X = Cl⁻, m = 0

M = Hg(II), X = Br⁻, m = 0

M = Cu(II), Pt(II), X = Cl⁻, m = 2

M = Cu(II), X = Br⁻, m = 1, and

Fe₂(SB)Cl₆ and Ru₂(SB)Cl₆.H₂O

Compounds of the category are characterized by the incorporation of the chloride or the bromide ions as ligands. These ions are known to have a great tendency towards bridging metal atoms to form di- or oligonuclear species. This does not preclude the possibility of bridging by the Schiff base ligand itself, but rather supplements it. The Schiff base may utilize

three N atoms (two imine and one pyridine nitrogens) which are sterically favourable to hold a metal atom, leaving the two quinoline nitrogens free to bond to another metal atom, thus forming a binuclear coordination compound. Suggestion of actual structural formulae for any of these compounds remains speculative in the absence of X-ray structure determination, which could not be realized because of the failure to isolate single crystals of any of these compounds.

(c) Trinuclear compounds as in the case of $\text{Rh}_3(\text{SB})_2\text{Cl}_9 \cdot m\text{H}_2\text{O}$, where $m = 3$ or 8 ; $\text{Ru}_3(\text{SB})_2\text{Cl}_9 \cdot 2\text{H}_2\text{O}$; $\text{Zn}_3(\text{SB})_2\text{Cl}_6 \cdot 6\text{H}_2\text{O}$; $\text{Cu}_3(\text{SB})_2\text{Cl}_6 \cdot 6\text{HO}$ and $\text{Cu}_3(\text{SB})_2\text{Br}_6 \cdot 2\text{H}_2\text{O}$.

We observe that in this category too, chloride or bromide ions may be involved as bridging ligands. Chloride bridges are common in Ru(III); Rh(III) and Cu(II) multinuclear species.

(d) A unique platinum compound has been isolated having the formula $\text{Pt}(\text{SB})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. This formula involves SB as a monodentate species. This may be explained by suggesting that SB exists in the anti-anti configuration. The two pairs of N atoms, which originally belonged to 8-aminoquinoline are blocked from coordination each by a water molecule held to them by hydrogen bonding. The remaining N atom (originally belonging to the pyridine moiety) is used in bonding Pt to the SB which now behaves as a monodentate ligand.

Conclusion

The condensation of 8-aminoquinoline with 2,6-pyridinedicarboxaldehyde can be effected either directly or in the presence of a suitable metal ion. In the latter case a Schiff-base complex is obtained that will decompose releasing the Schiff-base upon treatment with aqueous KCN solution. The Schiff-base reacts with transition metal salts to afford mono-, bi- or tri-nuclear complexes. It acts as a polydentate chelating agent in virtue of its 5 potential donor N atoms.

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