

The Synthesis of Polymeric Schiff Base Metal Complexes with 4 N Ligands

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Abstract

The bifunctional aldehyde 3,3'-diamino-4,4'-diformyldiphenyl-sulfone was prepared and reacted with diamines to Schiff bases. Polymeric metal complexes were obtained with Mn^{2+} , Ni^{2+} , Pd^{2+} , Pt^{2+} , Ir^{3+} and Au^{3+} . The thermal stabilities of these complexes are reported.

Introduction

Recently, polymeric Schiff base metal complexes found renewed interest as adsorbent materials [1–4]. It was also shown that in these polymeric complexes metal ions of second and third row transition elements could be stabilized [5, 6], which do not react easily with monomeric Schiff base ligands. All the polymeric Schiff base complexes synthesized so far are derivatives of salicyl aldehyde-containing OH-groups as complexing ligands. By substitution of the softer base $-NH_2$ instead of $-OH$, one should expect that complexation of large and soft metal ions should be even more easy. So far only some monomeric Schiff base complexes with *o*-aminobenzaldehyde [7–13] α -pyrrole-aldehyde [7] and *o*-amino-benzophenone or *o*-aminoacetophenone [14–16] were synthesized, but only once were metal ions [Pd^{2+} , Pt^{2+}] other than first-row transition elements complexed [14]. On the other hand, polymeric complexes with 4 N ligands have been prepared with porphyrine and phthalocyanine systems [17–20], but there exists only one report on salt-like polymeric Schiff base complexes of Co^{2+} and Ni^{2+} obtained from 2,6 diacetyl-pyridine, diamines and metal salts [21].

Experimental

Synthesis of 3,3'-diamino 4,4'-diformyldiphenyl-sulfone

Bifunctional salicylaldehydes may be easily obtained by a condensation reaction of salicylaldehyde with trioxane, aromatic aldehydes or H_2SO_4 [22, 23]. This reaction is not applicable to *o*-amino- or *o*-nitro-benzaldehydes, because the nitro-group de-

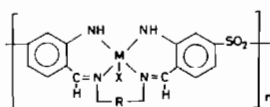
activates the aromatic system, as does the amino-group after the inevitable protonation.

But the compound 3,3'-dinitro-4,4'-diformyldiphenyl-sulfone is already known [24]. It can be obtained by: (a) reacting toluene at 180 °C with 93 per cent H_2SO_4 to *p*-ditolyl-sulfone [25], which is (b) nitrated in conc. H_2SO_4 solution under cooling with an ice bath with HNO_3 to 3,3'-dinitro-*p*-ditolyl-sulfone [26]; (c) the methyl groups of this compound are oxidized with *p*-nitrosodimethylaniline in the presence of Na_2CO_3 to the anile, which can be (d) hydrolysed with aqueous hydrochloric acid to the dialdehyde [24]. (c) is the most critical step of this synthesis. The reaction time is very long (more than 20 h), and the dianile cannot be obtained in a pure state by recrystallisation processes. The only way to get the pure dianile is a separation of the pyridine solution by column chromatography on Al_2O_3 . Thus, production of larger amounts is a very tedious process, and we have not found any improvement for this procedure.

The nitro-groups of 3,3'-dinitro-4,4'-diformyldiphenyl-sulfone can be reduced to amino-groups by the usual method for the synthesis of aromatic amino aldehydes [27, 28]. 720 mmol $FeSO_4$ dissolved in water are heated on a water bath. During rapid stirring, 40 mmol of dialdehyde and 200 ml concentrated NH_3 are dropped simultaneously into the vessel. The mixture is stirred for one more h. After cooling down in the water bath, the black iron sludge is separated and the solution is evaporated *in vacuo*, the brownish-yellow residue is dissolved in $CHCl_3$ and precipitated with petroleum ether. After recrystallizing from $CHCl_3$ /petroleum ether, the bright yellow product is pure. Yield: 60%. Molecular weight: 308 and 310 (theor. 304,32), m.p. 158 °C. *Anal.*: C: 55.35 (55.25), H: 3.91 (3.97), N: 9.11 (9.20) (theoretical values in brackets); soluble in chloroform, ethanol and diethylether.

Synthesis of the Schiff Bases and Complexes

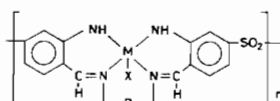
The Schiff bases are obtained from 3,3'-diamino-4,4'-diformyldiphenyl-sulfone and diamines in a minimum amount of the solvent mixture (dimethylformamide and trichlorobenzene 2:1) under continuous removal of the water formed by azeotropic distillation with benzene or toluene. As diamine,

TABLE I. Analytical Data for Complexes^a:

M	R	X	C	H	N	M
Mn ²⁺	-(CH ₂) ₄ -		48.59(51.8)	4.12(4.34)	14.80(13.42)	-(13.16)
Ni ²⁺	-(CH ₂) ₂ -		51.25(49.90)	4.14(3.66)	14.68(14.52)	-(15.24)
Ni ²⁺	-(CH ₂) ₄ -		49.59(52.33)	4.70(4.39)	13.81(13.56)	12.45(14.21)
Ni ²⁺	CH ₂ (cyclo C ₆ H ₁₀) ₂ -		58.10(59.57)	5.92(5.92)	10.40(10.92)	-(10.78)
Pd ²⁺	-(CH ₂) ₄ -		46.8(46.9)	3.7(3.9)	10.7(12.15)	21.8(23.1)
Pt ²⁺	-(CH ₂) ₄ -		38.08(39.34)	3.07(3.30)	8.33(10.19)	-(53.50)
Ir ³⁺	-(CH ₂) ₄ -	Cl	38.56(37.22)	3.50(3.11)	8.54(7.63)	-
Au ³⁺	-(CH ₂) ₄ -	Cl	38.04(36.84)	2.86(3.09)	9.07(9.54)	-(33.56)
U ⁶⁺	-(CH ₂) ₄ -	2 O	32.75(34.62)	2.38(2.90)	8.21(8.97)	-(38.1)

^aTheoretical values in brackets.

TABLE II. Thermal Stabilities for Complexes:



M	R	X	colour	thermal stability (°C)		
				in air	in Ar	difference
Mn ²⁺	-(CH ₂) ₄ -		light brown	260	300	40
Ni ²⁺	-(CH ₂) ₂ -		violet	280	305	25
Ni ²⁺	-(CH ₂) ₄ -		violet	260	275	15
Ni ²⁺	CH ₂ (cyclo C ₆ H ₁₀) ₂ -		violet	280	310	30
Pd ²⁺	-(CH ₂) ₄ -		orange brown	230	245	15
Pt ²⁺	-(CH ₂) ₄ -		dark brown	235	255	20
Ir ³⁺	-(CH ₂) ₄ -	Cl	dark brown	280	295	15
Au ³⁺	-(CH ₂) ₄ -	Cl	dark green	290	305	15
U ⁶⁺	-(CH ₂) ₄ -	2 O	yellow	280	315	35

1,4-diaminobutane was used throughout; in the case of Ni²⁺, complexes with ethylenediamine and 4,4'-diamino-dicyclohexylmethane were prepared additionally.

For preparation of the complexes, the hot solution of the Schiff base is mixed with a molar amount of metal salt (or its ammoniate) dissolved in DMF. An immediate change of colour is observed, which—analogue to findings for monomeric complexes [29]—may be due to formation of a +2-cation complex. To get the neutral complex the solution is cooled to 60 °C and treated with the strong base K⁺-tert-butylate. Normally the complex begins to separate after 30 min and its precipitation is complete after 12 h. The complex is sucked off, washed with DMF and methanol, treated with MeOH in a Soxhlet apparatus for 24 h, and dried *in vacuo* at 150 °C. In the case of the Mn²⁺ complex, strict exclusion of O₂ is mandatory throughout the operations. Yields are 40–60%. The analytical data are compiled in Table I.

Thermal Stability

20 mg of the finely powdered complexes were heated with a rate of 2 °C/min up to 700 °C, either in air or in an Ar atmosphere. The decomposition temperatures are given as the point where a loss of weight was observed, and are reported in Table II. In an inert gas atmosphere, stabilities are *ca.* 10% higher than in air. This indicates that in the latter case the first step of decomposition may be an oxidative attack. The Pd²⁺ and Pt²⁺ compounds are the least stable complexes, whereas the Au³⁺ complex is the most stable in air.

IR Spectra

IR spectra were recorded for all the compounds. The overall spectra are rather complex, especially for the polymeric compounds, and cannot be assigned properly. However, some characteristic bands may be mentioned. The ν_{SO} of the bridging SO₂ group are invariably at *ca.* 1300 and 1150 cm⁻¹ for the amino-

aldehyde, the Schiff bases and all the complexes. Two ν_{NH} are observed for the amino aldehyde at 3450 and 3340 cm^{-1} , which shift to 3405 cm^{-1} and 3250 cm^{-1} in the Schiff bases. After complexation only one ν_{NH} can be found at 3325 to 3380 cm^{-1} , indicating that only one H is left on the nitrogen atom. $\nu_{\text{C=N}}$, at 1630 cm^{-1} in the Schiff bases is shifted by complexation to ca. 1600 cm^{-1} . These latter findings are in agreement with the observations for analogous monomeric Schiff bases and their metal complexes [15]

Results and Discussion

We succeeded in preparing a ligand system analogous to the well-known [1–6, 22, 23] Schiff bases obtained from 5,5-methylene-bis-salicylaldehyde and diamines, but with NH_2 -groups instead of OH, so that 4 N ligands are present for complexation. It is shown by some model reactions that this ligand system is well suited not only for first row transition metal ions like Ni^{2+} and Mn^{2+} , but especially for larger and softer ions of higher transition rows. Thus, not only are Pd^{2+} and Pt^{2+} complexed more easily than with salicylaldehyde Schiff bases, but we were also able to synthesize for the first time polymeric complexes of Ir^{3+} and Au^{3+} . Thermal stabilities are about the same than found for polymeric salicylaldehyde-Schiff base complexes [5, 6, 22, 23]. The high thermal stability of the newly-prepared Au^{3+} complex is remarkable.

Unfortunately all the complexes are amorphous and are completely insoluble. Thus, structure investigations were not possible so far. Even for monomeric complexes only the structure of one Co^{2+} compound is known from X-ray diffraction data [30]. Co^{2+} is on top of a very flat square pyramid, i.e. the environment is approximately planar. The same planarity was deduced for monomeric Ni^{2+} complexes from spectroscopic data [11]. The identical colours of our polymeric complexes indicate that at least the Ni^{2+} (and probably also the Pd^{2+} and Pt^{2+}) complexes may also have the 4 N atoms in a planar arrangement.

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