SYNTHESIS AND CHARACTERIZATION OF Fe(III), Co(II), Ni(II), Cu(II) AND Zn(II) COMPLEXES WITH N-SALICYDENE-o-HYDROXYMETHYLENEANILINE

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Abstract—The new Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with tridentate Schiff base, the product of condensation of *o*-aminobenzyl alcohol with salicylaldehyde have been synthesized and characterized by elemental analysis, IR, electronic, EPR and Mössbauer spectra, thermal analysis, magnetic susceptibility and molecular weight measurements. Dimeric or polymeric structures for the investigated complexes were proposed. The interaction of the cobalt complex with dioxygen is also described.

The complexes of Cu(II), Fe(III), Ni(II) and other transition metals with potentially tridentate Schiff bases (Fig. 1) have attracted much attention. Most of them are dimers, although monomeric, trimeric or tetrameric forms are also known. The ligand can act both as dibasic tridentate or monobasic bidentate.¹ The interest has been focused mainly on magnetic properties of these compounds. In particular antiferro- and ferromagnetic coupling in Cu(II) complexes have been thoroughly investigated.²

We have undertaken the present study of the Schiff base complex derived from salicylaldehyde and *o*-aminobenzyl alcohol H₂HMPS (R = o-CH₂Ph), as a part of our efforts to synthesize the Co(II) complexes with attached free —OH groups being able to form an H-bond with a coordinated O₂ molecule. We have found that cobalt(II) complexes with HMPS react reversibly with dioxygen in the presence of amine, and for better understanding of coordinating properties of the ligand we have extended our study to complexes with other metals.

EXPERIMENTAL

Reagents

Salicylaldehyde was obtained from LOBA-Chemie, anthranilic acid from POCH-Gliwice



Fig. 1. General formula of potentially tridentate Schiff bases derived from salicylaldehyde and aminoalcohols.

and triethylamine from LABORCHEMIE-Apolda. Metal salts and solvents for synthesis were reagent grade. *o*-Aminobenzyl alcohol was obtained from anthranilic acid by electrochemical reduction.³ Solvents for spectroscopic measurements were purified before use.

Physical measurements

Electronic spectra in solution and diffuse reflectance spectra were recorded on a Beckman UV 5240 spectrophotometer, ESR spectra on a Jeol JES-Me $3 \times$ spectrometer (X-band). IR spectra were taken on a Perkin–Elmer 180 IR spectrometer using KBr pellets and Nujol mulls. Magnetic susceptibilities (80–300K) were measured by the Gouy method using HgCo(SCN)₄ as calibrant. Diamagnetic corrections were calculated using Pascal constants. Thermal analyses were done on a MOM Derivatograph Q 1500 D. Molecular weight measurements were performed in benzene by cryoscopic

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methods. Mössbauer spectra were recorded at room and liquid nitrogen temperatures as described in ref. 4. ¹H NMR spectra were recorded on a 100 MHz Tesla BS 567A spectrometer.

Preparation of ligand

Solutions of salicylaldehyde (0.05 mol) in 20 cm³ of methanol and *o*-aminobenzyl alcohol (0.05 mol) in 30 cm³ of methanol were mixed together and refluxed for 30 min. After cooling the yellow crystalline precipitate was filtered off and recrystallized from methanol. Yield *ca.* 80%. M.p. 124°C (literature data⁵ 126–128°C). Analytical data are given in Table 1.

Preparation of complexes

[FeLCl]₂. Solutions of FeCl₃ (0.005 mol) in methanol (15 cm³) and H₂L (0.005 mol) in methanol (15 cm³) were mixed together and triethylamine (0.01 mol) was added. The black crystalline complex precipitated immediately. It was separated, washed with methanol and dried over calcium chloride. Yield 90%. The compound is practically insoluble in non-coordinating solvents and sparingly soluble in DMF and pyridine.

 $[CoL(H_2O)_2]_2$. A solution of cobalt acetate tetrahydrate (0.005 mol) in methanol (20 cm³) was added to the hot solution of H_2L (0.005 mol) in methanol (20 cm³). The solution turned deep red, then triethylamine (0.01 mol) was added. The orange-red precipitate settled down. This was separated, washed with methanol and dissolved in a minimum amount of hot CHCl₃. The solution was filtered off and the complex was reprecipitated by addition of methanol, washed with methanol and dried in a stream of nitrogen. Yield 75%.

All operations were carried out under a nitrogen atmosphere in Schlenk apparatus. The same product was obtained with a 2:1 ligand to metal ratio.

The orange-red complex is easily soluble in noncoordinating solvents such as CHCl₃, toluene and benzene as well as in deoxygenated pyridine and DMF.

[CoL]_n. Bissalicylaldehydato cobalt(II) dihydrate (0.005 mol) was suspended in boiling toluene (200 cm³). Addition of *o*-aminobenzyl alcohol (0.01 mol) caused the suspension to dissolve. The red-brown solution was refluxed for 2 h and then the solvent was slowly evaporated for 3 h until the volume reduced to 30 cm³. The brown-red crystalline product that gradually formed was filtered off, washed with toluene and methanol, and dried in a stream of nitrogen. Yield 40%. All operations were carried out under nitrogen.

The compound is insoluble in non-coordinating solvents, but it dissolves slowly in deoxygenated DMF and pyridine.

[NiL(H₂O)₂]₂. (a) H₂HMPS (0.005 mol) and nickel acetate tetrahydrate (0.005 mol) were dissolved in boiling methanol (30 cm³) and then triethylamine (0.01 mol) was added. A green precipitate formed which was separated and recrystallized from CHCl₃/CH₃OH mixture. The product was dried in a stream of air. The same product was obtained with a 1:2 metal to ligand ratio.

(b) Bissalicylaldehydato nickel(II) dihydrate (0.005 mol) was suspended in boiling toluene. o-Aminobenzyl alcohol (0.01 mol) was added and the mixture was refluxed for 2 h. The complex was precipitated from the olive solution by the addition of *n*-heptane. Yield 75%.

 $[CuL]_n$. Copper(II) acetate hydrate (0.005 mol) was dissolved in boiling methanol (50 cm³) and a hot solution of H₂L (0.005 mol) in methanol (30 cm³) was added. The green complex precipitated almost immediately. This was then filtered off, washed with hot methanol and dried over calcium chloride in a desiccator. Yield 70%.

[Zn—L]. The compound was obtained in a similar way to the Ni(II) complex according to method (a). Yield 60%.

RESULTS AND DISCUSSION

[FeLCl]₂

Analytical data gave a 1:1:1 metal to ligand to chlorine ratio (Table 1). As shown by thermal analysis, there is no loss of weight until 260°C. Diffuse reflectance spectrum of [FeLCl]₂ gave no information about the geometry of the Fe(III) environment because the weak, spin-forbidden d-d transitions are completely covered by the tail of the very intensive CT band reaching nearly into the IR. A similar situation is observed for the complex solution in DMF with a CT band at 35,100 cm⁻¹ and a shoulder at *ca.* 27,800 cm⁻¹.

Magnetic susceptibility corresponds to a highspin Fe(III) ion with magnetic moment equal to 4.52 BM at room temperature, and clearly indicates the antiferromagnetic coupling with the exchange integral -2J = 33 cm⁻¹, calculated for a binuclear model.

The well resolved IR spectrum of $[FeLCl]_2$ shows absorption at 1607 cm⁻¹, characteristic of the coordinated —C=N— group. This indicates that the ligand is present in the Schiff base form, while investigations of the free ligand in solution suggested that it exists mainly in the benzoxazine form in

Compound	%C	%H	%N	%M	%Cl	vC==N	vCO_{ph}	$v CO_{alk}$
[FeLCl] ₂	53.2	3.6	4.2	16.5	10.9	1607	1540	1019
	(53.1)	(3.5)	(4.4)	(17.6)	(11.2)			
[FeL]	56.2	3.9	4.6	19.0		1607	1535	1029
$[CoL(H_2O)_2]_2$	52.5	4.3	4.4	19.0	_	1607	1533	1031
	(52.5)	(4.7)	(4.4)	(18.4)	_			
[CoL]"	59.0	3.5	4.6	19.9		1608	1528	1029
	(59.2)	(3.9)	(4.6)	(20.7)				
$[NiL(H_2O)_2]_2$	52.7	4.4	4.4	18.8		1607	1532	1041
	(52.6)	(4.7)	(4.4)	(18.4)				
$[CuL]_n$	59.1	4.1	5.0	21.7	—	1608	1528	1020
	(58.2)	(3.9)	(4.9)	(22.0)				
[ZnL]	44.9	3.4	3.2	21.6		1611	1531	1028
H ₂ L	73.9	5.8	66.1		_	1620	1506	1034
	(74.0)	(5.7)	(6.2)					

Table 1. Elemental analysis and IR data (in cm⁻¹) of investigated compounds

tautomeric equilibrium with the Schiff base.⁵ The band at 1540 cm⁻¹ is connected with the phenolic C—O stretching vibration and appears in the region characteristic for a coordinated phenolic group. The position of this band indicates that phenolic oxygen is not the bridging atom, because in phenoxo bridged compounds the C—O stretching vibration is shifted to a higher frequency.⁶ Some of the other bands may be tentatively assigned as follows: 3050, 760 cm⁻¹—aromatic C—H, 2850, 2930 cm⁻¹—CH₂ stretching, 1490 cm⁻¹—CH₂ scissors, 1580, 1467 cm⁻¹—C=C aromatic, 1019 cm⁻¹—alkoxy C—O stretching.

The Mössbauer spectrum of the complex measured at room temperature shows well resolved quadrupole splitting with QS = 0.832mm s⁻¹ and IS = 0.598 mm s⁻¹ {relative to $Na_{2}[Fe(CN)_{5}NO] \cdot 2H_{2}O\}$ confirms the presence of high-spin Fe(III). The intensity of the two lines are not equal, with the peak-height ratio I - /I + = 1.38and $\Gamma - = 0.341$, $\Gamma + = 0.466$ mm s⁻¹, while the integral intensities of both lines are the same. At 80K the spectrum is much more symmetrical with $QS = 0.848 \text{ mm s}^{-1}, IS = 0.697$ mm s⁻¹. $\Gamma - = 0.343,$ $\Gamma + = 0.365$ mm s^{-1} and I - /I + = 1.03. The observed asymmetry of the spectrum at room temperature probably arises from spin relaxation effects observed for penta-coordinated Fe(III)⁷ or for Fe(III) complexes with the strong antiferromagnetic coupling. Increasing the thermal population of the higher electronic states (which have longer relaxation times than the ground state) increases the overall relaxation time and causes the broadening of one line.

The magnetic properties and stoichiometry of the compound indicate a dimeric structure with alkoxo bridges.⁸ The Mössbauer parameters and J value

are similar to those of the complex $[Fe(SALPA)Cl]_2$ (R = --(CH₂)₃--), which has a dimeric structure with two alkoxy bridges and two Cl atoms axially coordinated to the Fe ion.⁹ The analogous structure is proposed for the present complex $[FeLCl]_2$ (Fig. 2).

We were also successful in preparing presumably the Fe(II) complex using a similar method as for $[CoL(H_2O)_2]_2$, starting from FeCl₂. This compound, isolated as a black precipitate, turned into a redbrown one (assigned as FeL in Table 1) within less than 1 min when exposed to air. A Mössbauer spectrum for the latter compound with IS = 0,622and $QS = 0.971 \text{ mm s}^{-1}$ indicates the presence of only one high-spin Fe(III) complex. The magnetic properties of this complex show an antiferromagnetic interaction ($\mu_{\text{eff}} = 2.81$ BM at 82K and 3.64 BM at 298K), however the plot of magnetic susceptibility vs temperature does not fit to any curve calculated from the dimeric model, so more than one kind of magnetic interaction between the Fe(III) centres could be predicted.

$[CoL(H_2O)_2]_2$

The analytical data (Table 1) and the 10.3% weight loss (theoretically 11.2%) at about 110° C



Fig. 2. Proposed structure for [FeLCl]₂.

indicates a 1:1:2 metal to ligand to H_2O ratio. The experimental molecular weight of 560 ± 30 daltons (mean value of three independent measurements) suggests the presence of the dimeric form.

The IR spectrum of $[CoL(H_2O)_2]_2$ is similar to that of $[FeLCI]_2$ in the region 700–1700 cm⁻¹ (Table 1) and similar assignments may be made. Again the position of the phenolic C—O stretching band i.e. 1533 cm⁻¹ indicates the lack of phenoxy bridges. The weak and broad band at *ca*. 3260 cm⁻¹ may be attributed to a *v*-OH vibration of a coordinated water molecule. The broadening of this band may be caused by strong intermolecular H-bonds.

The electronic spectrum of $[CoL(H_2O)_2]_2$ in toluene exhibits two CT bands at 34,480 and 25,640 cm⁻¹ and a *d*-*d* band at 10,150 cm⁻¹ with a shoulder at *ca*. 7810 cm⁻¹ (Fig. 3) which may be assigned to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition in pseudo-octahedral Co(II).¹⁰ The ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition is probably masked by an intensive CT band at 25,640 cm⁻¹. The spectra of $[CoL(H_2O)_2]_2$ in the solid state and $CHCl_3$ solution with bands at 10,050 and 10,200 cm⁻¹ respectively are similar to that of toluene solution. The magnetic moment of 4.9 BM (over the temperature range 82-298K) is typical for the highspin Co(II) in a pseudo-octahedral environment.¹⁰

On the basis of the above results and elemental analysis the dimeric structure with two alkoxy bridges and two water molecules coordinated to each Co atom is proposed. The similar dimeric structure for the Co(II) complex with HMPS was postulated by Syamal,¹¹ although he suggested two phenolic, not alkoxy bridges.

The electronic spectra of $[CoL(H_2O)_2]_2$ in DMF (13,700 and 5430 cm⁻¹) (Fig. 3) do not resemble the simple spectra of octahedral, tetrahedral or squareplanar Co(II) complexes. The low-energy bands in the 5260–7150 cm⁻¹ region, as well as the higher molar extinction coefficients indicate that pentacoordinated complexes are present in pyridine and DMF solutions. However, electronic spectra of square pyramidal or trigonal bipyramidal Co(II) complexes are not diagnostic enough to enable prediction of the exact geometry of the complex.¹²

When the oxygen is passed through the deoxygenated pyridine solution of $[CoL(H_2O)_2]_2$, the solution darkens, the band at 25,640 cm⁻¹ shifts to 25,000 cm⁻¹ and its intensity declines. A new shoulder appears at *ca.* 21,280 cm⁻¹ which is characteristic for dioxygen complexes of Co(II).¹³ These changes may be reversed by prolonged passage of inert gas through the solution. Complex solutions in non-coordinating solvents, such as toluene, also bind dioxygen reversibly after addition of amines such as pyridine or piperidine.

The characteristic EPR spectra of these systems (Fig. 4) obtained for the frozen solution indicate the existence of end-on superoxo complexes of Co(II)



Fig. 3. Electronic spectra of Co(II) complexes: $[CoL(H_2O)_2]_2$ in pyridine (1), DMF (3) and toluene (4); $[CoL]_n$ reflectance spectrum (2).



Fig. 4. EPR spectrum of the [CoL(H₂O)₂]₂-piperdine-O₂ system in frozen toluene/dichloromethane mixture at 77K.

in low temperatures,¹⁴ although μ -peroxo complexes may also be present. There is indirect confirmation of the existence of such binuclear diamagnetic species in liquid solutions. At room temperature there is no EPR signal for the complex solution containing the nitrogen base admixture. However after addition of I₂ or other oxidants, a well resolved 15-line EPR signal appears (g = 2.03, A = 13.0 G) which is characteristic for dimeric μ -superoxo complexes, products of oxidation of μ -peroxo complexes.

The experimental anisotropic EPR parameters for a monomeric dioxygen adduct (Fig. 4) $(g_1 = 2.098, g_2 = 2.01, g_3 = 1.99, A_1 = 25.0,$ $A_2 = 13.5, A_3 = 16.5$ G) are significantly different from those obtained for cobalt complexes with tetra- and bidentate Schiff bases¹⁵ or with porphyrins.¹⁶ They are rather similar to the EPR parameters of dioxygen adducts derived from Co(II) complexes with pentadentate Schiff bases.¹⁷ In the latter group of complexes dioxygen is coordinated in the trans position to the phenolic oxygen of the salicydene residue. The experimental EPR parameters are however not the spin-Hamiltonian ones because of the low symmetry of the dioxygen adducts, so computer simulation is necessary.¹⁸ This is why we do not present here a detailed interpretation of EPR data.

[CoL],

Thermal analysis revealed no loss of weight until 270°C. Diffuse reflectance spectrum of $[CoL]_n$ exhibits two bands at 8850 and 4950 cm⁻¹ with a

shoulder at 5320 cm⁻¹ (Fig. 3), as well as an intensive CT band at *ca*. 25,000 cm⁻¹ with a weak shoulder at *ca*. 17,400 cm⁻¹. The band at 8850 cm⁻¹ occurs in the range typical for ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}$ transitions of octahedral Co(II) complexes . On the other hand, the low-energy band at 4950 cm⁻¹ is indicative of the presence of penta-coordinated Co(II).¹² Magnetic moments equal to 5.1 BM at room temperature and 5.6 BM at 82K indicate a weak ferromagnetic interaction between Co(II) centres.

The complex dissolves slowly in DMF and pyridine giving the same electronic spectra as $[CoL(H_2O)_2]_2$ solutions in the same solvents. Similarly, when $[CoL]_n$ solutions in coordinating solvents are exposed to oxygen, one can observe the same EPR spectra as for $[CoL(H_2O)_2]_2$. These data suggest that the $[CoL]_n$ structure is broken upon solvolysis.

The band positions in the IR spectrum of $[CoL]_n$ are generally similar to that of $[CoL(H_2O)_2]_2$ (Table 1), except it is lacking the v-OH absorption, although the striking feature of the $[CoL]_n$ spectrum is the splitting of some bands. The alcoholic C—O absorption consists of two bands at 1029 and 1040 cm⁻¹, and the phenolic C—O absorption is split into two equal peaks at 1528 and 1544 cm⁻¹. The shift of the latter is commonly assigned to the bridging group.⁶ This splitting of some IR bands may arise from the fact that the ligand exists in two different forms in this compound. A tetrameric structure, consistent with the above data is proposed (Fig. 5), although the higher polymeric structures cannot be excluded.



Fig. 5. The proposed structure for [CoL]_n.

$[NiL(H_2O)_2]_2$

The bright green complex turns red-brown on heating at *ca.* 115° C, which is accompanied with the loss of 10.8% in weight. This is close to 11.2% calculated for the loss of two water molecules per one Ni atom.

The electronic spectrum of $[NiL(H_2O)_2]_2$ in CHCl₃ exhibits the CT bands at 33,300 and 24,400 cm⁻¹. The bands at 16,390 and 10,750 cm⁻¹ with a shoulder at 8510 cm⁻¹ (Fig. 6) occur in the range typical for distorted octahedral Ni(II) complexes and may be assigned to the spin-allowed transitions ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{2g}(F)$ and ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$. The third spin-allowed transition ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(F)$, expected in the region near 25,000 cm⁻¹ is not observed due to the very intensive charge-transfer band. Apart from spin allowed transitions ${}^{3}A_{2g} \rightarrow {}^{1}E_{2g}$. The magnetic moment of the complex equal to 3.23 BM is typical for octahedral Ni(II) complexes.

The electronic spectra of $[NiL(H_2O)_2]_2$ in CHCl₃, toluene or in solid state are essentially the same, while the spectra in DMF (16,400 and 11,360 cm⁻¹)

and pyridine (ca. 16,000 and 10,500 cm⁻¹) solutions, although still typical for octahedral Ni(II) complexes, vary in band positions (Fig. 6). The IR spectrum of $[NiL(H_2O)_2]_2$ is almost identical with that of $[CoL(H_2O)_2]_2$, even in the "fingerprint" region, so the same assignments were made.

The above data are in accordance with the dimeric structure analogous to that proposed for $[CoL(H_2O)_2]_2$. The electronic spectra of pyridine and DMF solutions indicate that solvent molecules coordinate to the Ni(II) ion, replacing water molecules and/or breaking the alkoxy bridges.

$[CuL]_n$

Thermal analysis for this complex demonstrates no loss of weight until 235°C and elemental analysis agrees with a 1:1 metal to ligand ratio (Table 1). The IR spectrum shows no v-OH band and is very similar to that of Fe and Co complexes in the region 700–1800 cm⁻¹. Magnetic moments of 1.62 BM at 82K and 1.85 BM at 298K indicates some extent of antiferromagnetic interaction between Cu centres.

 $[CuL]_n$ gives no EPR signal in the solid state or in DMF and toluene solutions, neither at room nor at liquid nitrogen temperature, while pyridine and 1-methylimidazole solutions give spectra typical for monomeric Cu(II) (for frozen pyridine solutions $A_{11} = 166$ G, $g_{11} = 2.257$). We explain this behaviour by assuming the polymeric structure of the complex with interaction between Cu(II) centres causes a very short spin-spin relaxation time, and hence the absence of the EPR signal. The polymeric



Fig. 6. Electronic spectra of [NiL(H₂O)₂]₂.

structure is destroyed when the complex is dissolved in coordinating amines and monomeric species form.

All the above results suggest non-monomeric nature of the complex, however we are not able to state how many Cu(II) centres it contains.

[Zn—L]

The complex lost 5% in weight at *ca*. 100°C. The IR spectrum exhibits broad, weak *v*-OH absorption at *ca*. 3340 cm⁻¹ and the other band positions are almost identical with that of cobalt or nickel complexes, except for small changes in the "finger-print" region.

The ¹H NMR spectrum of [Zn—L] in DMSOd₆ with azomethine produces a proton resonance at 8.5 ppm (s, 1H), an aromatic proton multiple peak centred at 7.25 ppm (m, 8H), and a CH₂ peak at 4.4 ppm (s, 2H). This clearly indicates the existence of the Schiff base form. It should be noted that the NMR spectrum of the free ligand in DMSO-d₆ [8.85 (s, 1H), 7.35 (m, 8H), 5.05 (m, 1H), 4.65 (d, 2H), 3.2 ppm (m, 1H)] or CDCl₃ [8.6 (s, 1H), 7.3 (m, 8H), 4.85 ppm (s, 1H)] does not confirm the existence of the postulated benzoxazine form.⁵

The NMR spectrum of [Zn-L] in CDCl₃ [8.1 (s, 1H), 7.0 (m, 8H), 4.85 (s, 2H) ppm] differs from that of the DMSO-d₆ solution; apart from the shift of the resonances, the peaks are much broader and less accurately resolved. The broadening of the peaks probably arises from the polymeric structure of the complex dissolved in CDCl₃. In DMSO solution the polymeric structure of the complex is destroyed and a new complex with coordinated DMSO is formed.

Although it seems that the type of coordination of the ligand in [Zn-L] is the same as in Co, Ni or Cu complexes, we are not able to propose any definite formulation consistent with the analytical data.

CONCLUSIONS

The similarity of IR spectra indicates the same coordination mode for the ligand in all investigated complexes. Under the synthesis conditions applied for the complexes under study, the H_2HMPS has a strong tendency to act as a dibasic tridentate ligand and forms non-monomeric complexes. This tend-

ency is reflected by the fact that the alcoholic OH group is deprotonated and coordinates to the metal even when the only base in the system is the salicylaldehyde anion derived from the starting $M(sal)_2 \cdot 2H_2O$.

It is noteworthy, that [FeLCl]₂ has magnetic properties similar to [Fe(SALPA)Cl]₂,⁹ while magnetic, the properties of the Cu complex of our ligand and SALPA are quite different. The reason for this may be the greater sensitivity of the magnetic properties to geometrical factors for bridged Cu(II) complexes than for those of Fe(III).^{2,8}

The studies on colbalt(II) complexes with HMPS and their interaction with dioxygen are being continued.

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