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Transition Metal Compounds containing Substituted Imidazole Ligands and Substituted Phenoles as Anions

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The synthesis and characterisation of a number of compounds with the general formula $M(RIz)_2(sf)_2(H_2O)_n$ *is described. The metal ions M are Co(II), Ni(II), Cu(II) and Zn(II), RIz stands for N-methylimidazole, 2-methylimidazole and 1,2-dimethylimidazole, whereas sf stands for the substituted phenolate anions* o-NO_2*-phenolate,* p-NO_2*-phenolate, 2,4,6-trichloro phenolate and 2-methoxyphenolate;* $n = 0$ *(usually) or 1.*

The coordination geometries around the metal ions have been determined by a combination of spectroscopic and magnetic methods. For the cobalt compounds geometries based on octahedral, tetrahedral and five-coordination have been found, whereas the nickel compounds have an octahedral geometry. For copper a tetragonal geometry is proposed. The esr spectra of the compound $Cu(NMI_2)_2(pnf)_2$ *(with pnf =* p-NO_2*-phenolato) indicate a dimeric species, most probably with phenolato oxygen atoms as bridging ligands. The magnetic exchange coupling between the copper ions is antiferromagnetic, as deduced from the* θ *value of* -18 *K in a Curie–Weiss plot (40–300 K).*

In all cases the phenolate oxygen atoms coordinate towards the metal ion, with additional donor atoms coming from the imidazoles and the other possible donor atoms from the ligands or, in a few cases, water.

Introduction

Recent evidence indicates that two tyrosine oxygens and three nitrogens, at least two of which are donated by histidine, are involved in the coordination polyhedron around the metal ion in the Fe(III)-transport protein transferrine [1]. Many papers on the coordination of transition-metal ions in metalloproteins have dealt with model coordination compounds containing tyrosine and histidine, but only in a few cases have crystal structure determinations elucidated the detailed geometry around the metal ion [2–4].

Because an investigation on model compounds containing these types of ligands could be very useful in providing insight into the geometry of naturally-occurring metalloprotein molecules, we started with a study on the complex formation of the 2,4,6-trichlorophenolate anion (tcf) and some imidazoles with Ni(II), Co(II), Cu(II) and Zn(II) as metal ions [5]. Spectral data of the imidazole (IzH), dimethylimidazole (DMIz) and N-methylimidazole (NMIz) Ni(II) and Co(II) complexes show a five-coordinated metal ion, whereas the Cu(II) compounds seem to have tetragonal geometry. This has been confirmed by X-ray structure determinations of $Co(NMIz)_2(tcf)_2$ and $Cu(IzH)_2(tcf)_2H_2O$ [2, 3].

We now continue these investigations by studying the complex formation of 2-methylimidazole (2MIz: this ligand possesses a sterically-hindered donor atom and has also a possibility to form hydrogen bonds with the phenolates) with tcf as anion and Ni(II), Co(II) and Zn(II) as metal ions. Another kind of compound has been prepared, using the same metal salts and imidazoles but with other phenolate anions. As a second phenolic ligand 2-methoxyphenol (mof) was selected, because of its easy deprotonation and the possibility of coordination to the metal ion through the methoxy oxygen. The ligand *o*-nitrophenol (onf) was used because the chelate part is isoelectronic with the strongly chelating ligand acetylacetone [4]. The fact that the *p*-nitrophenolate anion (pnf) also coordinates to the metal ion was interest-

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TABLE I. Analytical Data of Compounds $M(RIz)_2(sf)_2$.[a]

Formula	%C		%H		%N		%M		Melting point (°C)	Powder Isomorphism (X-ray)	Colour
	calc.	found	calc.	found	calc.	found	calc.	found			
$Co(NMIz)_2(mof)_2$	56.3	55.6	5.5	5.5	11.9	11.5	12.6	12.6	200	–	green
$Co(DMIz)_2(mof)_2$	57.9	56.9	6.0	6.0	11.3	10.9	11.8	11.4	133	–	green
$Co(2MIz)_2(tcf)_2H_2O$	37.8	37.9	2.8	2.8	8.8	8.8	9.3	9.2	148	–	blue
$Zn(2MIz)_2(tcf)_2$	37.5	37.6	2.8	2.8	8.8	8.6	10.2	10.1	152	–	white
$Ni(NMIz)_2(pnf)_2H_2O$	46.4	46.8	4.3	4.1	16.2	16.3	11.4	11.3	>250	A	yellow-green
$Co(NMIz)_2(pnf)_2H_2O$	46.4	47.0	4.3	3.9	16.2	16.3	11.4	11.5	226	A	orange
$[Cu(NMIz)_2(pnf)_2]_2$	47.8	47.4	4.0	4.0	16.7	16.6	12.6	12.7	205	–	green
$Ni(NMIz)_2(onf)_2$	48.1	48.2	4.0	4.2	16.8	16.9	11.8	11.7	192	B	dark-green
$Co(NMIz)_2(onf)_2$	48.1	47.9	4.0	4.1	16.8	16.9	11.8	11.8	185	B	brown-red
$Cu(NMIz)_2(onf)_2$	47.8	47.5	4.0	4.1	16.7	16.6	12.6	12.4	159	–	brown

[a] sf = substituted phenolate; other abbreviations: see text.

ing, first to compare the coordination compounds with the onf compounds, and also because a *p*-substituted phenolic compound shows more resemblance with the amino acid tyrosine. The recently reported [4] X-ray crystal structure of $Co(onf)_2(NMIz)_2$ demonstrating the chelation of metal ions by the nitrophenolate group was a useful basis for the interpretation of our results.

Experimental

Preparation of the Compounds

All the imidazoles, the metal salts, 2,4,6-trichlorophenol, *p*-nitrophenol and *o*-nitrophenol were commercially available and were used without further purification. The 2-methoxyphenolate compounds were synthesized by stirring for several hours a suspension of one mol of $Co(mof)_2xH_2O$ in a solution of two mol of the imidazole in acetone. $Co(mof)_2$-xH_2O was prepared by adding a solution of 0.02 mol mof in 100 ml 0.2 molar NaOH to a solution of cobalt sulfate (0.01 mol) in 50 ml H_2O.

The compounds containing 2,4,6-trichlorophenol or *o*-nitrophenol were obtained by slow evaporation of acetone from a mixture of water and acetone, containing 0.01 mol metal(II) sulfate, 0.02 mol tcf or onf, 0.02 mol imidazole, 0.02 mol NaOH, 200 ml H_2O and 400 ml acetone. Any precipitate formed during the mixing process was filtered off before the evaporation of the acetone was started. Crystallisation occurred after most of the acetone had evaporated. The *p*-nitrophenolate complexes were prepared by adding hot metal(II) sulfate solution (0.01 mol in 30 ml H_2O) to a solution of the *p*-nitrophenolate (0.02 mol) and N-methylimidazole (0.02 mol) in 100 ml of a 0.02 molar NaOH solution at 80 °C. After crystallisation all compounds were filtered, washed with a mixture of water and acetone, and dried *in vacuo* (1 mm Hg) at 30 °C.

Analyses

The metal content of all complexes was determined by standard complexometric titration. In addition, hydrogen, carbon and nitrogen analyses were carried out in our laboratory and at the Organisch Chemisch Instituut, TNO, Utrecht.

Physical Measurements

Infrared spectra were recorded on a Perkin-Elmer 297 Infrared Spectrophotometer in the 4000–600 cm^{-1} region as KBr discs. Far-infrared spectra (450–100 cm^{-1}) were obtained using a Beckman IR720 interferometer samples were recorded as pressed polythene discs, using pure polythene as a reference. Diffuse reflectance spectra were obtained on a Beckman DK2 spectrophotometer fitted with a reflectance attachment (35000–4000 cm^{-1}). EPR spectra were obtained using Varian Instruments and Q-band frequencies. X-ray powder diagrams of the compounds were obtained using a Guinier type powder camera and Cu-Kα radiation.

Magnetic susceptibility measurements were obtained in the 2–300 K region, using a Faraday balance and a PAR vibrating sample magnetometer. $HgCo(NCS)_4$ was used as a calibrant.

Results and Discussion

General

From all possible combinations of Ni, Co, Cu and Zn sulfates with the four imidazoles (IzH, DMIz, 2MIz and NMIz) and the four phenolate derivates, only the compounds listed in Table I could be obtain-

TABLE II. Ligand-field Maxima and EPR Data of Compounds $M(RIz)_2(sf)_2$.

Compound	Band maxima (unassigned)			
$Co(NMIz)_2(mof)_2$	21.9sh 20.8	16.4	8.9sh 7.3	
$Co(DMIz)_2(mof)_2$	21.7sh 21.3	16.6	8.4sh 7.4	
	$^4T_1(P) \leftarrow {}^4A_2$[c]	$^4T_1(F) \leftarrow {}^4A_2$[c]		
$Co(2MIz)_2(tcf)_2H_2O$	16.9	8.3 6.6sh		
$Co(2MIz)_2(tcf)_2H_2O$ (2.2 mmol/l in acetone)	17.2 (440)[a]	8.3 (55)[a]		
		$^4T_{2g} \leftarrow {}^4T_{1g}$[d]		
$Co(NMIz)_2(pnf)_2H_2O$	C.T. transition	8.5		
$Co(NMIz)_2(onf)_2$	C.T. transition	8.5		
	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$^3T_{2g} \leftarrow {}^3A_{2g}$[d]		
$Ni(NMIz)_2(pnf)_2H_2O$	15.8	9.5		
$Ni(NMIz)_2(onf)_2$	16.0	9.2		
	band maxima	$g_\perp$	$g_\parallel$	D (cm^{-1})
$[Cu(NMIz)_2(pnf)_2]_2$	14.7	2.10	2.22	0.09 (±0.01)
$Cu(NMIz)_2(onf)_2$	13.6	2.09	2.28[e]	-

[a]Molar extinction coefficient in acetone. [b]C.T. = charge transfer. [c]Assuming tetrahedral geometry. [d]Assuming octahedral geometry. [e]$A_\parallel$ = 160 Gauss.

ed as well-defined compounds, in addition to those mentioned in ref. 5. The analytical data, melting points, colour and isomorphism of the new compounds are reported in Table I. X-ray powder isomorphism was observed only for the Co and Ni compounds with the (*para-* and *ortho-*)nitrophenolate anions. Table II gives the ligand-field and EPR spectral data. Of the listed compounds the preparation and the crystal structure of *cis*-bis-(N-methylimidazole)bis(*o*-nitrophenolato)cobalt(II) has been reported during the course of this investigation [4].

The green $Ni(NMIz)_2(pnf)_2H_2O$ compound first crystallises as the anhydrous compound (yellow) but after some time it takes one water molecule from the atmosphere. From the change of the colour and the ligand-field parameters it is concluded that the water molecule is coordinated to the Ni(II) ion. It was not possible to remove the water molecule *in vacuo* (1 mg Hg) at 100 °C. The dehydration of $Co(NMIz)_2(pnf)_2H_2O$ was also not possible without decomposition of the product.

Considering the melting points of the compounds it is observed that the melting point of the *o*-nitrophenolate complexes is significantly lower than that of the *p*-nitrophenolate compound. Also the decreasing sequence Ni > Co > Cu usually observed appears to hold for all ligands. Relatively low melting points are an indication of a monomeric nature of complexes. A listing of the observed far-IR spectra is made in Table III, with some tentative assignments. The assignments in these metal phenolate compounds agree with the picture obtained from ligand-field spectra, isomorphism and the X-ray structure determination, [4]. The IR spectra in the region 4000–600 cm^{-1} indicate that all absorptions can be assigned to the phenolate anion and the coordinated NMIz, 2MIz or DMIz ligand. The presence of water in some compounds has been confirmed by recording IR spectra as nujol mulls between KBr windows.

The Nickel Compounds

The infrared spectrum and the elemental analysis of $Ni(NMIz)_2(pnf)_2H_2O$ show an anhydrous product

TABLE III. Far-IR Spectra (cm^{-1}) of the Compounds with a Few Tentative Assignments.

Compound	Ligand vibrations	M–O stretch	M–N stretch	Other vibrations
$Co(NMIz)_2(mof)_2$	287m	268s	230s(3)[a]	
$Co(DMIz)_2(mof)_2$	287s	272s	216m(3)	
$Co(2MIz)_2(tcf)_2H_2O$	382s(3)[a] 298s 196s	332s	260s	190s
$Zn(2MIz)_2(tcf)_2H_2O$	380s(3) 298s 198s	332s	252s	176s
$Ni(NMIz)_2(pnf)_2H_2O$	392s 182m	310s	250s(2)	
$Co(NMIz)_2(pnf)_2H_2O$	390s 180m	305s ,	232s	
$[Cu(NMIz)_2(pnf)_2]_2$	392m 185m(2)	380s(2)	295s(4)	231m
$Ni(NMIz)_2(onf)_2$		310s	264s	245s
$Co(NMIz)_2(onf)_2$		312m	264m	234s
$Cu(NMIz)_2(onf)_2$		320s	282s	

[a]Number of band maxima with the centre at the listed band maximum.

directly after the preparation, but a hydrated compound after a few days. The hydrated and the water-free compound are further characterised by their ligand-field spectra, which show the characteristic bands for a Ni(II) ion in an octahedral geometry. The band position at 8.3 kK and 15.1 kK, for the anhydrous compounds (not in the table) and 9.5 and 15.8 kK for the hydrated product are in agreement with octahedrally based cations having a chromophore $Ni(O_4N_2)^{2+}$. The hydration of the complex appears to increase the ligand-field strength. Also the ligand-field parameters of $Ni(NMIz)_2(onf)_2$ (9.2 and 16.0 kK) agree with a pseudo-octahedral surrounding of the Ni(II) ion. X-ray powder isomorphism with the cobalt *o*-nitrophenolate compound and very similar IR spectra, together with the known crystal structure of the cobalt compound [4] confirm this geometry.

The Copper Compounds

The EPR spectra (Table II) show a typical two g-value spectrum, and both $g_\parallel$ and $g_\perp$ are split evenly into (super) hyperfine components. $g_\parallel$ is split into four lines, whereas $g_\perp$ has a super hyperfine $A_\perp$. The parameters are close to those Cu(II) compounds having 4 strongly coordinating ligands. The g values for both Cu compounds indicate a similar kind of distortion from octahedral.

The spectral data of $Cu(NMIz)_2(onf)_2$ are in agreement with a tetragonal coordination geometry, consisting most likely of two N-atoms of N-methylimidazole and two oxygen atoms of the phenolic group. Additional weak coordination in the axial direction from NO_2 groups of neighbouring molecules cannot be excluded.

The ESR spectrum of $Cu(NMIz)_2(pnf)2$ in the solid state is clearly indicative of a dimeric species, as deduced from the so-called half-field signal (Δm = 2) and the zero-field splitted signal in the Δm = 1 region [6]. The calculated zero-field splitting parameters and g-values (obtained from both X-band and Q-band frequencies according to the literature [6, 7]) are given in Table II. The values are in the usual range for ligand-bridged copper(II) systems [6, 8].

To investigate the nature of the magnetic coupling between the copper ions, magnetic susceptibility measurements of the powdered compound were recorded between 2 and 300 K. It appears that the susceptibility in the region 40–300 K follows the Curie–Weiss law, with a θ value of −18 K indicating antiferromagnetic exchange. However, below 40 K the susceptibility has a slightly different behaviour with a θ value of about −2 K, suggesting a weaker exchange at these temperatures. The origin for this can be either a phase transition at about 40 K at which the structure changes slightly (*e.g.* a different Cu–O–Cu angle), or the presence of a second exchange path (between dimers). Without knowledge of the crystal structure these two possibilities cannot be distinguished.

A frozen solution EPR spectrum of $Cu(NMiz)_2(pnf)_2$ in dmf shows the presence of a monomeric species only ($g_\parallel$ = 2.27, $A_\parallel$ = 175 G, $g_\perp$ = 2.04), indicative of a decomposition of the dimeric compound under these conditions.

The Cobalt Compounds

The ligand-field spectrum of $Co(2MIz)_2(tcf)_2H_2O$ is in agreement with a tetrahedral $Co(L)_4^{2+}$ species. The calculated ligand-field parameters are Dq = 490 cm^{-1} and B = 700 cm^{-1}. These values indicate that the ligands are relatively strongly bound to the Co(II) ion [9]. Since the corresponding Zn compound is IR-isomorphous with the cobalt trichlorophenolate compound, a tetrahedral coordination for both the Co and the Zn compound seems likely.

The ligand-field spectra of $Co(2MIz)_2(tcf)_2H_2O$ as a solid and as a solution of 2.2 mmol/l in acetone show only small differences, indicating the same chromophore both in the solid state and in solution.

The ligand-field maxima of the cobalt *o*-nitrophenolate and the cobalt *p*-nitrophenolate compound are identical. No ligand-field parameters can be calculated because an intense charge-transfer transition appears at 15.5 kK making the observation of σ^2 and σ^3 impossible. From the position of σ^1 at 8.5 kK for both compounds we suggest a coordination for the Co^{2+} ion in the *p*-nitrophenolate similar to that described in the crystal-structure determination of the *o*-nitrophenolate compound, but with O-donor atoms from neighbouring molecules.

The shape of the absorption bands and the position of the spectra of the methoxyphenolate Co(II) compounds resemble the spectra of other five-coordinated cobalt(II) ions. Molar extinction determination, or proton NMR spectroscopy of these compounds was not possible, because no suitable solvent for these compounds could be found.

Final Remarks

The result described in this investigation have shown that the combination of imidazole-type ligands and phenolate anionic ligands forms a variety of coordination compounds with first-row transition-metal ions. The obtained coordination geometry for a certain metal ion is dependent on the particular combination of imidazole ligand and phenolate anion. Future work in this area will deal with chelating ligands that have both the imidazole and the phenolate group built in one ligand, such as in dipeptides His–Tyr and Tyr–His.

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