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Transition Metal 2,4,6-Trichlorophenolates Coordinated by Imidazole, N-Methylimidazole and 1,2-Dimethylimidazole

R. C. VAN LANDSCHOOT, J. A. M. VAN HEST and J. REEDIJK*
Department of Chemistry, Delft University of Technology, P.O. Box 5045, 2600 GA Delft, The Netherlands

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The preparation and properties of a new series of transition-metal trichlorophenolato (tcf) compounds with Ni(II), Co(II), Cu(II) and Zn(II) as metal ions, and imidazoles as nitrogen ligands, are described. Most compounds have the general formula $M(tcf)_2(ligand)_2$*, whereas in a few cases* H_2O *is also bound in the crystals. The compound* $Ni(tcf)_2(imidazole)_6$ *is exceptional in containing uncoordinated trichlorophenolate ions, apart from the well-known octahedral* $Ni(imidazole)_6^{2+}$ *cation.*

The other Co(II) and Ni(II) compounds show electronic spectra that are different from the spectra known for regular six-coordinate and four-coordinate complexes. In fact most spectra agree with five-coordinate metal(II) ions. The Cu(II) ligand field and EPR spectra agree with tetragonal geometry.

Magnetic susceptibility measurements of the compounds indicate no magnetic exchange interactions, suggesting a monomeric character of the compounds. This monomeric character is confirmed by a molecular-weight determination in solution, and is further illustrated by the very good solubility in apolar solvents.

The infrared spectra of the compounds with 1,2-dimethyl imidazole and with N-methyl imidazole indicate isomorphism between the Co(II) and Zn(II) compounds, whereas the Ni(II) compounds show very similar spectra.

Introduction

The coordination of transition metal ions in metalloproteins by histidine and tyrosine amino-acid side chains is well documented [1], although the exact geometry around the metal ions is known in only a few cases [2].

Model coordination compounds containing this type of ligands could be of help in further understanding and elucidating the geometry in the naturally-occurring metalloproteins.

In the Fe(III)-transport protein, transferrine, both imidazole ligands and phenolic ligands are involved in the coordination polyhedron around the metal ion [3]. Therefore, an investigation was started on model coordination compounds containing these types of ligands.

As metal ions Co(II), Ni(II), Cu(II) and Zn(II) were selected because the coordination chemistry of these metal ions is well documented and because spectral and magnetic studies are easily performed for structural characterisation. As imidazoles were selected: imidazole (IzH), N-methylimidazole (NMIz; no hydrogen bonding) and 1,2-dimethylimidazole (DMIz; bulky group near the donor site). As a first phenolic ligand 2,4,6-trichlorophenolate was selected, because of its easy deprotonation. The final goal is to study tyrosine and histidine as a ligand.

The recently reported [4] X-ray structure of $Cu(tcf)_2(IzH)_2(H_2O)$ was a useful basis for the interpretation of our results.

Experimental

Preparation of the Compounds

All metal salts, imidazoles and 2,4,6-trichlorophenol (tcfH) were commercially available. A solution of Nickel, Cobalt, Copper or Zinc sulfate (0.01 mol) in 100 ml water and 50 ml acetone was slowly added to a solution of 0.02 mol 2,4,6-trichlorophenol and 0.02 mol N-base in 100 ml 0.2 molair NaOH and 100 ml acetone. Any precipitation during the mixing process was prevented by adding more acetone. Crystallization appears after a few days when a great deal of the acetone has evaporated. The compounds were filtered, washed with a mixture of water and acetone and dried at 30 °C *in vacuo* (1 mm Hg).

The NMIz and DMIz complexes of Ni(II) initially contained a few molecules of water. These compounds were evacuated at 80 °C (1 mm Hg) in order to remove the water.

For comparison purposes a compound $Cu(tcf)_2$ was prepared from $Cu(SO)_4)\cdot 6H_2O$, tcfH and NaOH as described above.

Analyses

The metal content of all complexes was determined by standard complexometric titration. In

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*Present address: Gorlaeus Laboratories, Dept. of Chemistry, State University of Leiden, P.O. Box 9502, 2300 Leiden, The Netherlands.

TABLE I. Analytical Data for Some Trichlorophenolato Nickel, Cobalt, Copper and Zinc Complexes.

Formula	%C		%H		%N		%M		Melting point (°C)	Isomorfism (IR)
	calc.	found	calc.	found	calc.	found	calc.	found		
$Ni(NMIz)_2(tcf)_2 \cdot 3H_2O$	35.9	36.5	3.3	3.4	8.4	8.0	8.8	8.8	decompose	–
$Ni(NMIz)_2(tcf)_2$	38.9	38.9	2.6	2.7	9.1	9.2	9.5	9.5	195	A'
$CO(NMIz)_2(tcf)_2$	39.0	39.6	2.6	2.7	9.1	8.8	9.5	9.5	158	A
$Cu(NMIz)_2(tcf)_2$	38.6	38.8	2.6	2.7	9.0	9.0	10.2	10.2	174	A'
$Zn(NMIz)_2(tcf)_2$	38.5	38.5	2.6	2.4	9.0	8.8	10.5	10.5	149	A
$Ni(IzH)_6(tcf)_2$	42.1	43.2	3.3	3.8	19.6	19.3	6.9	6.9	>230	–
$Co(IzH)_2(tcf)_2 \cdot H_2O$	35.6	35.6	2.3	2.2	9.2	9.2	9.7	9.7	189	–
$Cu(IzH)_2(tcf)_2 \cdot H_2O$	35.4	35.3	2.3	2.5	9.2	9.4	10.4	10.3	decompose	–
$Ni(DMIz)_2(tcf)_2 \cdot 4H_2O$	37.3	37.4	4.0	4.2	7.9	7.7	8.3	8.5	decompose	–
$Ni(DMIz)_2(tcf)_2$	41.0	40.9	3.1	3.1	8.7	8.7	9.1	9.1	212	B
$Co(DMIz)_2(tcf)_2$	41.0	42.4	3.1	3.5	8.7	8.3	9.2	9.2	181	B
$Cu(DMIz)_2(tcf)_2$	40.7	41.1	3.1	3.2	8.6	8.2	9.8	9.4	162	–
$Zn(DMIz)_2(tcf)_2$	40.6	40.9	3.1	3.2	8.6	8.5	10.1	10.1	169	B

addition hydrogen, carbon and nitrogen analyses were carried out, partly in our laboratory, partly at the Organisch Chemisch Instituut, TNO, Utrecht.

Physical Measurements

Infrared spectra recorded on a Beckman Acculab-6 in the 4000–250 cm^{-1} region as Nujol mulls between KBr plates and as KBr discs yield the same absorption spectra; so it can be assumed that the compounds do not decompose in the KBr discs. Diffuse reflectance spectra were obtained on a Beckman DK2 spectrometer fitted with a reflectance attachment (35000–4000 cm^{-1}). EPR spectra were performed on a Varian E4 instrument at X-band frequencies. The NMR spectra were recorded in deuterated acetone on a T-60 nmr spectrometer and X-ray powder diagrams of the compounds were obtained using a Guinier-type powder camera and Cu-Kα radiation. Low-temperature susceptibilities were performed on a PAR vibrating sample magnetometer in the 25–90 K region.

Results and Discussion

General

The compounds are listed in Table I together with their analytical data, melting point and infrared isomorfism. No X-ray powder isomorfism was observed. However, the infrared spectra of several pairs of compounds are very similar, suggesting more or less the same coordination of tcf and the imidazole in these groups of compounds. In Table II the ligand-field and EPR spectral data are presented. Of the listed compounds the preparation and the crystal structure of $Cu(IzH)_2(tcf)_2H_2O$ has been reported recently by Wong *et al.* [4]. All complexes are initially crystalline in character, but two of them, $Ni(NMIz)_2(tcf)_2 \cdot 3H_2O$ and $Ni(DMIz)_2(tcf)_2 \cdot 4H_2O$, became amorphous after losing water on suction *in vacuo* at 80 °C. From the colour change and the change of the ligand field parameters upon removal of the water, it is concluded that at least part of the water molecules are initially coordinated to the Ni(II) ions. The DMIz compound spontaneously loses some water molecules on standing in the air during some weeks. All dried complexes are readily soluble in chloroform and acetone without losing their spectroscopic properties, indicating the same molecular species both in the solid state and in solution. Considering the melting points of the compounds the usual decreasing sequence, Ni > Co > Zn appears. All relatively low melting points are an indication for a monomeric nature of the complexes.

Compounds Containing N-Methylimidazole

A comparison between the infrared spectra of $Co(NMIz)_2Cl_2$ [5], $Cu(tcf)_2$ (the only purely available tcf salt) and the spectra of the N-methylimidazoletrichlorophenolate complexes indicates that the absorption bands can be assigned to the trichlorophenolate anion and the coordinated N-methylimidazole ligand.

The absence of water is confirmed by the infrared spectra as Nujol mulls between KBr plates. Also the nickel compound, after drying at 80 °C *in vacuo* for 24 hours shows no presence of water. Initially $Ni(NMIz)_2(tcf)_2 \cdot 3H_2O$ shows broad absorptions at 2800–3400, 1230–1300 and 700–850 cm^{-1}.

The electronic d–d absorption spectrum of $Ni(NMIz)_2(tcf)_2 \cdot 3H_2O$, indicating an octahedrally-

TABLE II. Colour, Ligand-field Maxima and EPR Data of the Trichlorophenolato Compounds.

Compound	${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$ kK		${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ kK		${}^3T_{2g} \leftarrow {}^3A_{2g}$ kK		Colour
$Ni(NMIz)_2(tcf)_2 \cdot 3H_2O$	26.1		15.9	13.7 sh	9.4		green
$Ni(NMIz)_2(tcf)_2$	20.8		12.3	13.6 sh	6.8		yellow
$Ni(DMIz)_2(tcf)_2 \cdot 4H_2O$	25.6		15.1	13.6 sh	9.6		green
$Ni(DMIz)_2(tcf)_2$	21.7		12.4	13.4 sh	6.6		yellow
$Ni(IzH)_6(tcf)_2$	27.7		17.6	13.0 sh	10.9		light blue
	${}^4T_{1g}(P) \leftarrow {}^4A_{2g}$		${}^4T_{1g}(F) \leftarrow {}^4A_{2g}$				
$Co(IzH)_2(tcf)_2 \cdot H_2O$	18.4 sh	17.4	8.8				violet blue
	unassigned band maxima						
$Co(NMIz)_2(tcf)_2$	18.5	15.8	10.8	7.5	6.5		violet blue
$Co(NMIz)_2(tcf)_2$ 2.5 mmol/l in acetone	19.2(320)[d]	15.9(290)	11.4(30)	8.0(30)	6.8(30)		
$Co(DMIz)_2(tcf)_2$	18.9	15.9	12.3	8.3	6.7		violet
$Co(DMIz)_2(tcf)_2$ 2.5 mmol/l in acetone	18.6(380)[d]	15.9(340)	11.1(40)	7.8(50)	6.6(50)		
	band maxima			g or $g_\perp$	$g_\parallel$	A	
$Cu(NMIz)_2(tcf)_2$	23.0[a,b]	17.1 sh	13.5 sh	2.06	2.30	175G	brown
$Cu(DMIz)_2(tcf)_2$	22.6[a,c]		13.1 sh	2.05	2.26	173G	brown
$Cu(IzH)_2(tcf)_2 \cdot H_2O$	23.0[a]	16.8 sh	13.8 sh	2.12			brown

[a] C.T. transition. [b] 5×10^{-4} mol in acetone 23.0 kK ($\epsilon = 1600$). [c] 5×10^{-4} mol in acetone 22.6 kK ($\epsilon = 1720$). [d] Molar extinction coefficient.

surrounded Nickel(II) ion, is quite different from the spectrum of the dried product (Table II). The transitions at 6.8 kK and at 12.3 kK in the latter product are very unusual for six coordinated Ni(II) with relatively strong ligands. There is also no evidence for a D_{4h} symmetry, built by *e.g.* $[NiN_2O_2]$. A five-coordinate geometry might well be possible [6]. The ligand field spectra of $Co(NMIz)_2(tcf)_2$ as a solid and as a solution of 2.5 mmol/l in acetone are identical, indicating a single species in the solid state and in solution. The shape of the absorption bands and the positions of the spectrum of the cobalt compound resembles more or less the spectra of other five-coordinated cobalt ions [7]. Moreover, the observed molar extinctions are about 3 times smaller than observed for tetrahedral Co(II) [8].

$Zn(NMIz)_2(tcf)_2$ is isomorphous with the Co compound, but unfortunately, the Co and Ni compounds are not isomorphous.

A molecular-weight determination of the $Co(NMIz)_2(tcf)_2$ in acetone confirms the monomeric character of this compound.

Magnetic susceptibility measurements of the Nickel and Cobalt compounds at low temperatures show that no significant magnetic interaction between the metal ions occurs, again confirming the monomeric nature of the compounds. The values of μ_{eff} for the Ni compound (3.18 BM) and Co compound (4.35 BM in the 25–85 K region) are normal for the high-spin M(II) ions.

NMR experiments (in acetone-d_6) of NMIz, tcfH and $Co(NMIz)_2(tcf)_2$ and on mixtures of these three compounds indicate a rapid exchange of ligand molecules and anions. This phenomenon is well-known to be the case for Co(II) high-spin compounds.

Very recently [9], a crystal structure determination of $Co(NMIz)_2(tcf)_2$ has shown that indeed a five-coordinate structure occurs, with one of the Cl atoms as a weak fifth ligand.

Spectral data (Table II) for $Cu(NMIz)_2(tcf)_2$ are normal for tetragonal Cu(II) and agree with the reported X-ray structure.

Complexes with 1,2-Dimethylimidazole

The nickel compound initially crystallises with four molecules of water. The green product changes to yellow after losing water on suction *in vacuo* at 80 °C. These water molecules are also lost upon standing in the open air for a few weeks. From the IR spectra obtained as Nujol mull it is clear that the Nickel compound after drying – just as Ni(NMIz)$_2$(tcf)$_2$·3H$_2$O – has lost all its water. All IR absorptions are due to complexed 1,2-dimethylimidazole and the trichlorophenolate anion. IR isomorphism is observed for the dried Nickel, the Cobalt and the Zinc compounds.

The band maxima of the ligand-field spectra for Ni(DMIz)$_2$(tcf)$_2$·4H$_2$O indicate a distorted octahedral coordination. The dried Nickel compound shows similar band maxima as the corresponding N-methylimidazole complex, again suggesting a probably five-coordinate structure. The ligand-field spectrum of Co(DMIz)$_2$(tcf)$_2$ is similar as observed for Co(NMIz)$_2$(tcf)$_2$. A single monomeric species appears to be present both in the solid state and in solution.

The magnetic susceptibility measurements indicate a monomeric species for Co(DMIz)$_2$(tcf)$_2$, as deduced from the magnetic moment of 4.28 BM (40–90 K region).

The ligand-field spectrum of Cu(DMIz)$_2$(tcf)$_2$ is unusual in having the main low-frequency absorption at 13.1 kK which is below the values known for normal tetragonal CuN$_2$O$_2$ and CuN$_2$O$_2$X$_2$ systems. Probably steric effects of the 2-methyl group are responsible for this, just as found for Cu(DMIz)$_4$Cl$_2$ [10].

The solution UV–VIS spectra unfortunately are dominated by tail of the intense C.T. transitions at 22.6 kK, making the observation of d–d transitions impossible. On the other hand, the EPR spectra of the NMIz and the DMIz compounds (both in frozen acetone at 77 K) are almost identical, indicating that in this solution similar species must be present (see Table II).

Complexes with Imidazole

The compound [Ni(IzH)$_6$](tcf)$_2$ is unusual in that it contains trichlorophenolate anions which are not coordinated to the metal ion.

The ligand-field spectrum shows the three characteristic bands for an octahedrally surrounded Ni(II) ion [11]. The IR spectrum in the region 3500–2400 cm^{-1} (N–H stretchings) in fact is similar to that of the compound Ni(IzH)$_6$(HCOO)$_2$ [11]. From these data it can be concluded that a very strong hydrogen-bond interaction must occur between the N–H group and the trichlorophenolate anion.

The UV–VIS spectrum of the complex with formula Co(IzH)$_2$(tcf)$_2$·H$_2$O agrees with a distorted tetrahedral environment. The fact that this compound shows a different spectral behaviour compared with the other compounds must be related to the fact that imidazole still has an acidic N–H, capable for hydrogen bonding, or to the presence of the water molecule, which is very strongly bound in the lattice (just as found in case of Cu [4]). However, coordination of this water instead of one of the tcf anions cannot be ruled out.

A distorted octahedral coordination for bis-(2,4,6-trichlorophenolate)diimidazolecopper(II) monohydrate as suggested by the ligand field and EPR measurements is confirmed by the crystal structure determination reported by Wong *et al.* [4].

Final Remarks

The present study has shown that stable coordination compounds are formed between first-row transition-metal ions and a combination of imidazole ligands and 2,4,6-trichlorophenolate ions. For the Cu(II) compounds a tetragonal geometry seems most likely. In case of Co, Ni and Zn(II) and N-alkylated imidazoles a five-coordinated geometry is proposed; with unsubstituted imidazole tetrahedral Co(IzH)$_2$(tcf)$_2$ and octahedral [Ni(IzH)$_6$](tcf)$_2$ are formed.

Future studies will deal with other imidazoles (like histidine) and with other phenolic ligands (like tyrosine).

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