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Synthesis and Characterization of Cobalt(II), Nickel(II) and Copper(II) Chloride Complexes with Bis[(diphenylphosphinyl)methyl]phenylphosphine Oxide and Bis[(diphenylphosphinyl)methyl]-phosphinic Acid*

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A series of cobalt(II), nickel(II) and copper(II) chloride complexes with the tripode organophosphorous compounds: bis[(diphenylphosphinyl)methyl]phenylphosphine oxide (RPPh) and bis [(diphenylphosphinyl)methyl]phosphinic acid (RPOH) were studied. Complexes of the general stoichiometry $[M(RPPh)_3] [MCl_4] \cdot 4H_2O$ and $[M(RPOH)Cl \cdot nH_2O]_m$ (M = Co(II), Ni(II) or Cu(II); n = 0 — 4, m = 1, 2 or more) were isolated.

According to spectral and magnetic data, complexes with the RPPh ligand appear to have both an octahedral and a tetrahedral surrounding of the metal(II) ion.

For the complexes $[M(RPOH)Cl \cdot nH_2O]_m$ the electronic effect of the metal ion seems to be predominant. A tetrahedral surrounding for the cobalt(II) complex, an octahedral surrounding for the nickel(II) complex and a tetragonal distorted octahedral surrounding for the copper(II) complex has to be assumed.

INTRODUCTION

Chloride complexes of transition metals with organic bisphosphine oxides, that is ligands in which two phosphoryl groups are bridged by one or more methylene groups, have been reported.[1-7] The results obtained show that the ligands are capable of forming complexes with different coordination numbers and different coordination geometries, according to the nature of the metal ions.

Less attention has been paid to complex formation with tri and polydentate phosphine oxides.[8,9] Conformation analyses revealed that the tridentate phosphine oxide bis[(diphenylphosphinyl)methyl]phenylphosphine oxide acts preferentially as a bidentate ligand, but the coordination of all three phosphoryl oxygens to the metal ion is not excluded.[10] Our previous investigations of the formation of Zr(IV), Hf (IV), Co(II), Ni(II) and Cu(II) perchlorate complexes with the ligands

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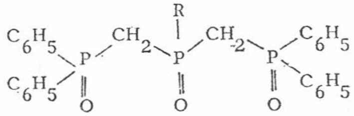
* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.



R=C_6H_5 . . . bis[(diphenylphosphinyl)methyl]phenylphosphine oxide (RPPh)
R=OC_2H_5 . . . bis[(diphenylphosphinyl)methyl]ethyl phosphinate (RPOEt)
R=OH . . . bis[(diphenylphosphinyl)methyl]phosphinic acid (RPOH)

indicated that in these complexes at least two P=O groups from one ligand were coordinated to the metal ion. However, in some of the complexes isolated the coordination of all three P=O groups to the metal ion had to be assumed.[11,12]

The work reported here was undertaken to obtain more information about the effect on coordination of the nature of the metal ion, the substituent R on the central phosphorus atom and the three bridged phosphoryl groups.

Cobalt(II), nickel(II) and copper(II) chloride complexes with bis[(diphenylphosphinyl)methyl]phenylphosphine oxide (RPPh) and bis[(diphenylphosphinyl)methyl]phosphinic acid (RPOH) were isolated and characterized.

RESULTS AND DISCUSSION

Complex Formation

The complexes were obtained by the reaction of ethanolic solutions of metal(II) chlorides with the ligands dissolved in absolute ethanol or dichloromethane. The isolated compounds are high spin, paramagnetic substances of various stoichiometries which depend on the nature of the metal(II) ion, on ligand properties and on the ligand to metal ratios used in the reaction mixture. All of the complexes isolated are of rather low solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, CCl_4 and $ClCH_2CH_2Cl$. This prevented measurement of their molecular weights. Dissolution in ethanol or methanol was, however, in most cases accompanied by changes in the colour of the solution with regard to the solid sample. Differences observed in the visible spectra of nujol mulls and ethanolic solutions of the complexes indicate changes in the environmental symmetry of the diluted complexes. Some of the complexes are soluble in nitromethane. IR spectra of recrystallized complexes were not identical to those recorded before recrystallization. The formation of a new type of complex has to be presumed.

Complexes Formed with RPPh

Cobalt(II) chloride reacts with an equimolar amount of RPPh in ethanolic solution forming $Co(RPPh)Cl_2 \cdot 2H_2O$. The corresponding nickel(II) and copper(II) complexes could not be isolated. By mixing an ethanolic solution of cobalt(II) or nickel(II) chloride with a dichloromethane solution of RPPh, or by mixing an ethanolic solution of copper(II) chloride with an ethanolic solution of RPPh in a metal to ligand ratio of 2 to 3, blue, green or yellow crystalline precipitates, respectively, were isolated. Analytical, spectral and magnetic data suggest that new metal complexes of the general type $[M(RPPh)_3][MCl_4] \cdot 4H_2O$ (M=Co(II), Ni(II) or Cu(II)) were formed.

Complexes Formed with RPOH

Regardless of the reaction ratios used, RPOH as a ligand forms only one type of complex with Co(II), Ni(II) and Cu(II) chlorides: $[M(RPOH)Cl \cdot nH_2O]_m$ (M = Co(II), n = 2; M = Ni(II), n = 4; M = Cu(II), n = 0, m = 1, 2 or more). All complexes were isolated by precipitation from ethanolic solutions. Cobalt(II) immediately after precipitation forms a rather unstable pink complex whose IR spectra show it to contain coordinated ethanol. After all the ethanol had been released, the blue stable $[Co(RPOH)Cl \cdot 2H_2O]_m$ was formed. According to X-ray powder pattern investigations, Co(II) and Ni(II) complexes are amorphous compounds, which can be an indication of a dimeric or polymeric structure. In contrast to Ni(II) and Co(II) complexes, the $[Cu(RPOH)Cl]_m$ complex is a substance with very well developed crystallinity.

Complex with RPOEt

We did not succeed in isolating metal(II) chloride complexes with RPOEt as ligand. Under drastic conditions (at elevated temperatures) according to the literature[13] the neutral phosphinic esters react with metal halogenides by releasing alkyl halogenides. Complexes identical to those precipitated with RPOH have been isolated.

Analytical data for all the complexes isolated are listed in Table I.

TABLE I

Summary of Analytical Data for the Complexes

Compound	Metal %		P%		Cl%		H_2O%	
	calc.	found	calc.	found	calc.	found	calc.	found
$Co(RPPh)Cl_2 \cdot 2H_2O$	8.19	8.51	12.91	12.92	9.85	10.29	5.00	5.39
$[Co(RPPh)_3] [CoCl_4] \cdot 4H_4O$	5.91	5.80	13.98	13.74	7.11	6.92	3.61	3.83
$[Ni(RPPh)_3] [NiCl_4] \cdot 4H_2O$	5.89	6.23	13.98	13.60	7.11	7.27	3.61	3.94
$[Cu(RPPh)_3] [CuCl_4] \cdot 4H_2O$	6.35	6.62	13.92	13.55	7.08	7.36	3.59	4.02
$[Co(RPOH)Cl \cdot 2H_2O]_m$	9.44	9.95	14.88	15.07	5.68	6.07	5.77	6.16
$[Ni(RPOH)Cl \cdot 4H_2O]_m$	8.89	8.89	14.07	13.87	5.37	5.92	10.91	10.81
$[Cu(RPOH)Cl]_m$	10.71	10.34	15.68	15.55	5.98	6.11		

Infrared Spectral Studies

The most important absorption bands in the spectra of the ligands and their complexes in the range 4000—200 cm^{-1} are those of P=O, P—O—(H), O—H, M—Cl and M—O vibrations.

The spectra of the ligands RPPh and RPOH exhibit at least three strong absorption bands in the range 1250 to 1155 cm^{-1} which are assigned to P=O stretching vibrations. In the spectra of the complexes these absorption bands are shifted to lower wave numbers, thus indicating coordination of the ligands through phosphoryl oxygens. According to the spectral data, the central P=O group is always involved in complex formation. The absorption band at 1250 cm^{-1} in the RPOH spectrum and the band at 1215 cm^{-1} present in the RPPh spectrum are absent in the spectra of the corresponding complexes. In the spectra of the complexes there arises in the P=O stretching region a rather broad band with one or two shoulders, which indicates a nonequivalency in the binding of the P=O groups. There is a possibility that some of them are in the exterior coordination sphere and are more weakly bound to the metal ion.[14] Free P=O groups in the complexes cannot be excluded. The spectra of $[M(RPPh)_3][MCl_4]\cdot 4H_2O$ exhibit broad bands with a maximum at 1170 cm^{-1} and a shoulder at 1195 cm^{-1} both attributed to P=O stretching vibrations. The shoulder at 1195 cm^{-1} is indicative of a free P=O group in the coordinated ligand. In the $Co(RPPh)Cl_2\cdot 2H_2O$ spectrum there appears a narrower band with a maximum at 1165 cm^{-1}.

In the spectra of the Co(II) and Ni(II) chloride complexes with RPOH there arise broad bands with maxima at 1160 cm^{-1} and two shoulders appearing at 1200 and 1190 cm^{-1}, assigned to P=O stretching vibrations. The $[Cu(RPOH)Cl]_m$ spectrum exhibits completely different P=O stretching vibrations with more very sharp bands and more or less shifted as compared to the P=O stretching vibrations of the ligand. The P=O vibration of the central P=O group is shifted to lower wave numbers (from 1250 to 1225 cm^{-1}) (Figure 1). The bands

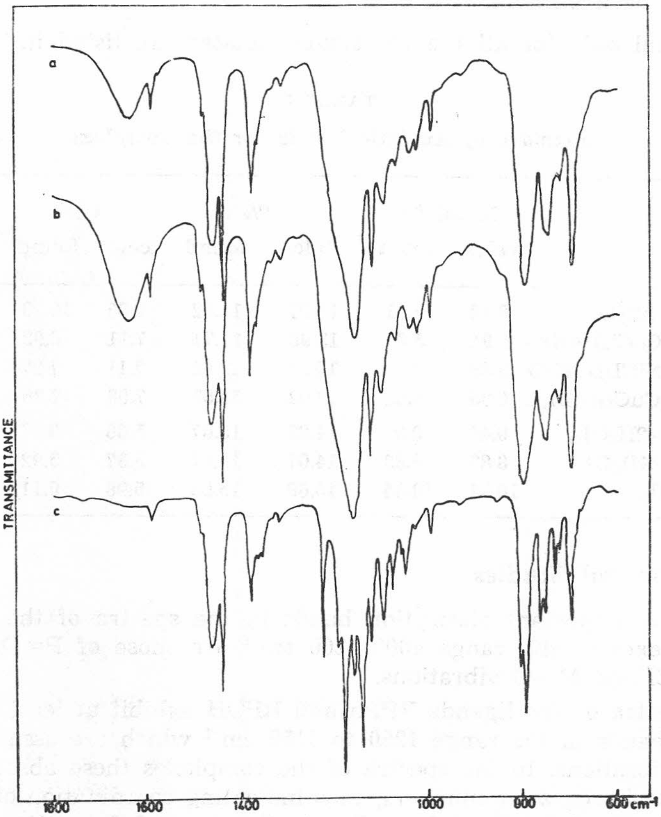


Figure 1. IR spectra of (a) $[Co(RPOH)Cl\cdot 2H_20]_m$; (b) $[Ni(RPOH)Cl\cdot 4H_2O]_m$; (c) $[Cu(RPOH)Cl]_m$ in the region of 1800—600 cm^{-1}.

appearing in the RPOH spectrum at 2600 and 2200 cm^{-1}, assigned to P(O)—OH vibrations perturbed by strong hydrogen bonding, and the strong band at 955 cm^{-1} attributed to P—O—(H) vibration,[15] are absent in the spectra of the corresponding complexes. These results indicate the coordination of both oxygens from the central phosphorus atom to the metal ion.

All spectra of the complexes apart from the spectrum of $[Cu(RPOH)Cl]_m$ exhibit two maxima at ~ 3400 and 1630 cm^{-1} assigned to O—H stretching and H—O—H bending modes from lattice or coordinated water molecules.[16] In the spectra of the unstable Co(II) chloride complex with RPOH, which was recorded immediately after isolation there appears a strong band at 3200 cm^{-1}. This band is due to the O—H stretching vibration of coordinated ethanol. After two days this maximum disappears and in the spectrum of the same complex there arise O—H stretching and H—O—H bending vibrations of lattice water.

Far IR spectra have been recorded for the ligands and all of the complexes in the range 600—200 cm^{-1}. The complexity of the spectra of ligands containing the phenyl groups makes detailed assignments rather difficult. Vibrations found in the far IR region include several phenyl ring vibrations, most of them designated as »X-sensitive«: P—C (phenyl) stretch (t); out-of-plane bending (y); in-plane ring rotation (u); out-of-plane ring bending (x) and weak, not X-sensitive, out-of-plane ring deformation (w).[17] Since our ligands contain a number of phenyl groups, these frequencies can interact and split. In addition δ (P—O) must be present. As a result both RPPh and RPOH have very rich far IR spectra with several sharp and strong bands. The spectrum of RPPh reveals strong bands at 550, 541, 514, 500, 463 and 411 cm^{-1} and bands of medium intensity at 434, 374, 340, 290 and 223 cm^{-1}. Two weak bands at 275 and 250 cm^{-1} are also present. RPOH has very strong and sharp absorption bands at 539, 509 and 412 cm^{-1}, medium to strong bands at 470, 460, 397 and 386 cm^{-1}, bands of medium intensity at 373 and 206 cm^{-1} and weak bands at 327 and 304 cm^{-1}. Comparing the spectra of the ligands and complexes, it is obvious that there occur many perturbations upon coordination. The ν (M—O) vibrations in the known phosphine oxide complexes are usually located in the free region of the ligand spectra[5b,9,18–20] in the range 450 to 400 cm^{-1}. In our case, regarding the rich ligand spectra, it is obvious that in the region from 550 to 350 cm^{-1} there exists an overlap between metal sensitive and ligand absorption bands. Therefore ν (M—O) vibration bands could not be assigned with complete certainty.

The spectra of $[Co(RPOH)Cl \cdot 2H_2O]_m$ and $[Ni(RPOH)Cl \cdot 4H_2O]_m$ are very similar to each other and much simpler than that of the free ligand. Two or three ligand bands are replaced by one rather broad band. In the spectra of the Co(II) and Ni(II) complexes appears a rather broad band with a maximum at 475 cm^{-1} which could tentatively be assigned as the ν (M—O) mode. The other possibility might be a shoulder appearing at 430 cm^{-1}. The spectrum of $[Cu(RPOH)Cl]_m$ is completely different with several new strong bands. The metal sensitive band is probably at 450 cm^{-1} (Figure 2).

The spectra of all RPPh complexes are rather similar. All the ligand bands are present and recognizable, but they are much wider and more or less shifted. In the range 420 to 430 cm^{-1} there arises a band which is much more intensive in the spectra of the complexes than in the free ligand. This band might be assigned as the ν (M—O) vibration mode.

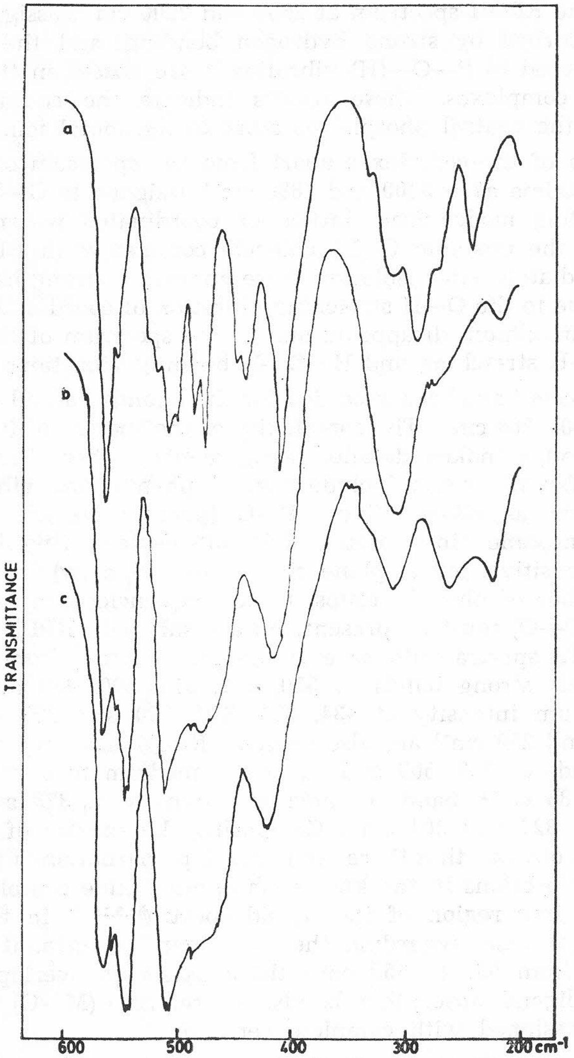


Figure 2. Far IR spectra of (a) $[Cu(RPOH)Cl]_m$; (b) $[Co(RPOH)Cl \cdot 2H_2O]_m$; (c) $[Ni(RPOH)Cl \cdot 4H_2O]_m$ in the region of 600—200 cm^{-1}.

In all spectra of the complexes there appears a new rather sharp band at 565 cm^{-1}. This is probably too high for ν (M—O), although in some amine oxide complexes this mode was found[21] to lie in the range 570 to 520 cm^{-1}.

M—Cl vibration assignments provided us with conclusive information about structural possibilities. In the region below 350 cm^{-1} only a few bands, mainly of low intensity, are present in ligand spectra. For all RPPh complexes ν (M—Cl) vibrations confirm the coordination number four.[16] $Co(RPPh)Cl_2 \cdot 2H_2O$ and $[Co(RPPh)_3] [CoCl_4] \cdot 4H_2O$ exhibit strong tetrahedral bands at 307 and 285 cm^{-1}. Absorption bands with maxima at 284 and 244 cm^{-1} are due to the distorted tetrahedral structure of the $NiCl_4^{2-}$ ion in $[Ni(RPPh)_3]$ $[NiCl_4] \cdot 4H_2O$. In the spectrum of $[Cu(RPPh)_3]$ $[CuCl_4] \cdot 4H_2O$ two bands were present at 294 and 265 cm^{-1} which are consistent with a distorted tetrahedral structure of the $CuCl_4^{2-}$ ion.

M—Cl vibrations of $[M(RPOH)Cl \cdot nH_2O]_m$ confirm various coordinations of the metal ions. $[Co(RPOH)Cl \cdot 2H_2O]_m$ exhibits a band at 306 cm^{-1} indicative of the tetrahedral environment of cobalt(II). In the spectrum of $[Ni(RPOH)Cl \cdot 4H_2O]_m$ the ν (Ni—Cl) band is not present above 200 cm^{-1}. That means that both the tetrahedral and the octahedral monomeric structure for this complex has to be excluded. As octahedral ν_b (Ni—Cl) vibrations lie below 200 cm^{-1} a polymeric octahedral structure could be expected. Cu—Cl vibrations maxima occur in $[Cu(RPOH)Cl]_m$ at 310 and 285 cm^{-1} indicative of a tetragonal distorted octahedral or planar structure of the complex.[22,23]

Bands assignments for ligands and complexes are listed in Tables II and III.

TABLE II

IR Spectra and Conductivity Data of the Ligands and Complexes

Compound	ν (P=O)/cm^{-1}	ν (O—H)/cm^{-1}	Λ_M
RPPh	1215 s, 1192 vs, 1163 s		
$Co(RPPh)Cl_2 \cdot 2H_2O$	1195 sh, 1165 vs	3400 m, br	2.87
$[Co(RPPh)_3]$ $[CoCl_4] \cdot 4H_2O$	1195 sh, 1170 vs	3440 m, br	5.63
$[Ni(RPPh)_3]$ $[NiCl_4] \cdot 4H_2O$	1195 sh, 1170 vs	3380 m, br	7.51
$[Cu(RPPh)_3]$ $[CuCl_4] \cdot 4H_2O$	1195 sh, 1170 vs	3380 m	23.25
RPOH	1250 s, 1180 s, 1155 s	2600 br, 2200 br	[illegible]
$[Co(RPOH)Cl \cdot 2H_2O]_m$	1200 sh, 1190 sh, 1160 vs	3380 m, br	1.43
$[Ni(RPOH)Cl \cdot 4H_2O]_m$	1200 sh, 1190 sh, 1160 vs	3360 s, br	3.07
$[Cu(RPOH)Cl]_m$	1225 s, 1190 sh, 1180 vs, 1160 s, 1140 vs		5.19
$Co(RPOH)Cl \cdot nC_2H_5OH$	1225 sh, 1200 s, 1190 s 1160 vs	3200 s	

TABLE III

Far IR Spectra of the Complexes

Compound	ν (M—C)/cm^{-1}	ν (M—O)/cm^{-1}
$Co(RPPh)Cl_2 \cdot 2H_2O$	307 s, 285 s	425 s
$[Co(RPPh)_3]$ $[CoCl_4] \cdot 4H_2O$	307 s, 285 s	420 s
$[Ni(RPPh)_3]$ $[NiCl_4] \cdot 4H_2O$	284 s, 244 s	420 s
$[Cu(RPPh)_3]$ $[CuCl_4] \cdot H_2O$	294 s, 265 s	420 s
$[Co(RPOH)Cl \cdot 2H_2O]_m$	306 s	475 s
$[Ni(RPOH)Cl \cdot 4H_2O]_m$	<200	475 s
$[Cu(RPOH)Cl]_m$	310 m, 285 s	450 s, sp

Conductivity Measurements

Conductivity measurements of metal(II) complexes were carried out at room temperature in 10^{-3} M nitrobenzene solutions.

The complexes $[M(RPOH)Cl \cdot nH_2O]_m$ (M=Co, Ni or Cu) and $Co(RPPh)Cl_2 \cdot 2H_2O$ had molar conductance values in the range 1—5 $cm^2\ \Omega^{-1}\ mol^{-1}$ showing the nonelectrolytic nature of these compounds. Λ_M value for $[Cu(RPPh)_3]\ [CuCl_4] \cdot 4H_2O$ was 23.35 $cm^2\ \Omega^{-1}\ mol^{-1}$, as expected for 1 : 1 electrolytes.[24] Values of 5.6 and 7.51 $cm^2\ \Omega^{-1}\ mol^{-1}$ obtained for complexes $[Co(RPPh)_3]\ [CoCl_4] \cdot 4H_2O$ and $[Ni(RPPh)_3]\ [NiCl_4] \cdot 4H_2O$, respectively, are somewhat high for nonelectrolytes, but too low for 1 : 1 electrolytes. Some sort of molecular association of these complexes in nitrobenzene solutions has to be presumed.[4]

Molar conductance values are listed in Table II.

TABLE IV

Electronic Spectral Data of the Complexes

Compound	Colour	λ_{max} (ε) (nm)	Medium	μ eff. (B.M.)
$Co(RPPh)Cl_2 \cdot 2H_2O$	blue	627 sh, 663 sh, 686 vs	nujol*	4.18
	blue	575 sh, 610 sh, 630 sh, 656 (91)	abs. ethanol	
$[Co(RPPh)_3]\ [CoCl_4] \cdot 4H_2O$	blue	532 sh, 616 sh, 633 sh, 663 sh, 688 vs	nujol*	4.95
	pink	480 sh, 520 (21.8)	abs. ethanol	
$[Co(RPOH)Cl \cdot 2H_2O]_m$	blue	530 sh, 600 sh, 620 sh, 632 sh, 677 vs	nujol*	4.91
	pink	553 (15.5)	abs. ethanol	
$[Ni(RPPh)_3]\ [NiCl_4] \cdot 4H_2O$	green	420, 655 s, 704 s	nujol*	3.71
		418 (25), 778 (12)	abs. ethanol	
$[Ni(RPOH)Cl \cdot 4H_2O]_m$	greenish-yellow	416, 680 sh, 785	nujol*	3.34
		420 (19.5), 690 sh, 774 (7.5)	abs. ethanol	
$[Cu(RPPh)_3]\ [CuCl_4] \cdot 4H_2O$	yellow	417, 1205	nujol*	2.06
$[Cu(RPOH)Cl]_m$	blue-green	830	nujol*	1.93
	pale-green	840 (31)	methanol	

* nujol mull

Electronic Spectral Data

Solid state (nujol mull) and solution electronic spectra for all of the complexes isolated were recorded. According to the spectral data, changes in the environmental symmetry of the complexes occur upon dissolution in ethanol.

The electronic spectra of the blue $Co(RPPh)Cl_2 \cdot 2H_2O$ complex exhibit in the 550—750 nm region a characteristic, multicomponent band associated with the $^4A_2 \rightarrow {}^4T_1(P)$ transition in tetrahedral symmetry. The close similarity of the solid and ethanolic solution spectra implies that the tetrahedral stereochemistry is retained in ethanolic solution. The solid state spectrum of $[Co(RPPh)_3][CoCl_4]\cdot 4H_2O$ also shows a very intensive band with a maximum at 688 nm and several shoulders (at 616, 633 and 663 nm) characteristic for the tetrahedral $CoCl_4^{2-}$ ion. The low intensity of the ν_3 transition band in the octahedral field of cobalt(II) did not allow exact assignment of this absorption. A band at ~530 nm is suspected. In ethyl alcohol, however, extensive solvolysis was observed and we could assign only a weak band corresponding to the octahedral Co^{2+} ion (at 520 nm). The same effect is shown by similar binuclear complexes containing MCl_4^{2-} ions.[3] Generally, it is known that the tetrahalo ions are very sensitive to solvolysis.[25]

Nujol mull spectra of the $[Ni(RPPh)_3][NiCl_4]\cdot 4H_2O$ complex show characteristic absorption bands for both octahedral and tetrahedral Ni(II) ions. The weak band above 400 nm is consistent with the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition in the octahedral ligands field, and the intensive one with maxima at 655 and 704 nm is characteristic for the tetrahedral $NiCl_4^{2-}$ ion.[25,26] Like the corresponding cobalt(II) complex, this compound is not stable in ethanol.

Absorption bands present in the solid state spectrum of the yellow copper (II) complex $[Cu(RPPh)_3][CuCl_4]\cdot 4H_2O$ at 417 and 1205 nm are consistent with a deformed tetrahedral structure of the $CuCl_4^{2-}$ ion.[27,28] The band corresponding to the $[Cu(RPPh)_3]^{2+}$, which occurs in the spectrum of the acetone solution of $[Cu(RPPh)_3](ClO_4)_2\cdot 4H_2O$ complex at 962 nm[12] is masked by the very broad near IR band of the tetrahedral Cu^{2+}.

The nujol mull electronic spectrum of $[Co(RPOH)Cl\cdot 2H_2O]_m$ is consistent with tetrahedral coordination of the central metal ion, according to the intensity, position and shape of the absorption band.[29] However, the complex dissolves in ethanol to give a pink solution. Consequently, the intensive band with a maximum at 677 nm disappeared gradually in ethanol and after some time only a band of low intensity at 553 nm, corresponding to octahedral symmetry of Co^{2+}, could be assigned. Obviously, an increase occurs in the coordination number of the cobalt(II) ion, probably by the attachment of two solvent molecules. The presence of the ethanol molecules is, as already said, confirmed by IR spectra.

Spectral data of the greenish-yellow complex $[Ni(RPOH)Cl\cdot 4H_2O]_m$ indicate the same stereochemistry in ethanolic solution and in the solid state and are typical of a nickel(II) complex in an octahedral environment.[29] The weak bands corresponding to the octahedral Ni^{2+} arise in the spectra at ~420 and ~780 nm.

The Cu(II) complex with RPOH, $[Cu(RPOH)Cl]_m$, exhibits a very broad asymmetric band at 830 nm (nujol mull) or 840 nm (methanol solution). Similar spectra were observed for a number of Cu(II) complexes which were characterized as tetragonally distorted octahedral.[29-31]

Magnetic Measurements

All complexes isolated are high spin paramagnetic substances. $Co(RPPh)Cl_2\cdot 2H_2O$ has a magnetic moment $\mu_{eff} = 4.18$ B. M. This value is consistent with the tetrahedral structure confirmed by far IR and visible spectral data.

$[Co(RPPh)_3]\ [CoCl_4]\cdot 4H_2O$ reveals a moment of 4.95 B. M. This value should be the square root of the mean of the squares of moments of $[Co(RPPh)_3]^{2+}$ and $[CoCl_4]^{2-}$ ions. In the corresponding perchlorate complex we found the magnetic moment for the $[Co(RPPh)_3]^{2+}$ ion to be $\mu_{eff} = 5.10$ B. M. For $[CoCl_4]^{2-}$ the moment of 4.69 B. M. was reported.[32,33] So, the obtained magnetic moment of 4.95 B. M. is in fair agreement with the root mean square value of the $[Co(RPPh)_3]^{2+}$ and the $[CoCl_4]^{2-}$ ions.

$[Ni(RPPh)_3]\ [NiCl_4]\cdot 4H_2O$ reveals a magnetic moment $\mu_{eff} = 3.71$ B. M. which agrees well with the square root average of moments determined for the Ni(II) ion in the tetrahedral $NiCl_4^{2-}$ ion ($\mu_{eff} = 3.92$)[32,33] and in the octahedral field (μ_{eff} for $[Ni(RPPh)_3](ClO_4)_2$ is 3.18 B. M.).[12] Copper(II) complexes $[Cu(RPPh)_3]\ [CuCl_4]\cdot 4H_2O$ and $[Cu(RPOH)Cl]_m$ have moments of 2.06 and 1.93 B. M., respectively, corresponding to the spin only moment of the d^9 configuration of the copper(II) ion. They are more or less independent of the stereochemistry. Values obtained for magnetic moments are given in Tables IV and V.

TABLE V

Magnetic Data for $[Co(RPOH)Cl\cdot 2H_2O]_m$ *and* $[Ni(RPOH)Cl\cdot 4H_2O]_m$

$[Co(RPOH)Cl\cdot 2H_2O]_m$				$[Ni(RPOH)Cl\cdot 4H_2O]_m$			
T (K)	X_g (.10^{-5})	X'_M	μ (B. M.)	T (K)	X_g (.10^{-5})	X'_M	μ (B.M.)
78.6	3.094	0.031808	4.79	74.58	3.0944	0.018547	3.40
105.6	4.007	0.025368	4.87	112.13	2.0818	0.012581	3.41
136.1	3.235	0.020554	4.93	158.85	1.4790	0.009045	3.43
176.2	2.587	0.016505	4.99	200.07	1.1864	0.007325	3.46
236.5	1.964	0.012621	5.01	257.68	0.9246	0.005784	3.48
293.9	1.564	0.010133	4.99	294.26	0.8218	0.005180	3.52

$\Theta\ [Co(RPOH)Cl\cdot 2H_2O]_m = -11$ $\Theta\ [Ni(RPOH)Cl\cdot 4H_2O]_m = -3$

calculated from $\mu = \sqrt{X'_M\,(T-\Theta)}$

Far IR and visible spectra indicate a tetrahedral surrounding for the Co^{2+} ion in $[Co(RPOH)Cl\cdot 2H_2O]_m$. However, it has a magnetic moment $\mu = 4.91$ B. M. which is the upper limit for a tetrahedral Co(II) complex. This surely means that some kind of distortion is present, though tetrahedral cobal(II) complexes which exhibit high magnetic moments have been reported.[5b,34]

$[Ni(RPOH)Cl\cdot 4H_2O]_m$ exhibits a moment $\mu = 3.34$ B. M. which corresponds to the octahedral coordination of the nickel(II) ion, confirmed by far IR and visible spectral data.

The octahedron is probably formed by a bridging halogen atom. The rather high moments are typical for tetragonally distorted complexes of this type. Such complexes regularly have moments in the range 3.35—3.45 B. M.[35] The temperature dependency of the magnetic susceptibility of [Co(RPOH)Cl·

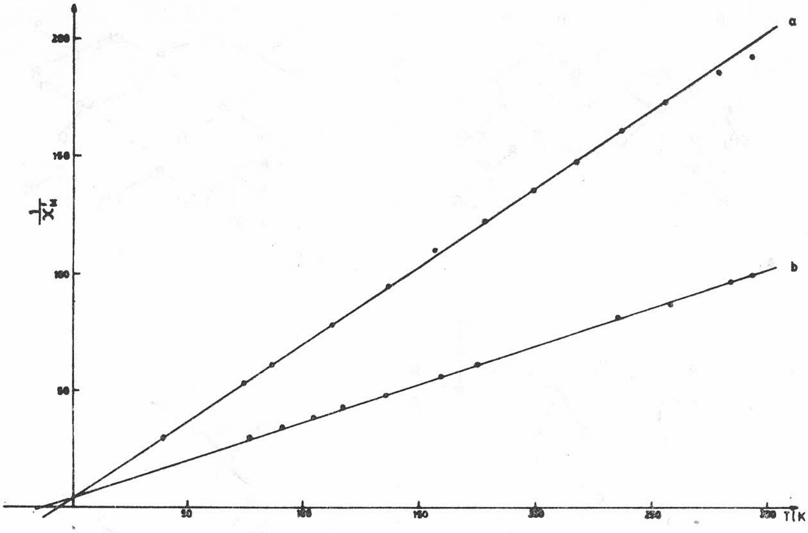


Figure 3. Temperature dependence of magnetic susceptibilities of (a) $[Ni(RPOH)Cl \cdot 4H_2O]_m$; (b) $[Co(RPOH)Cl \cdot 2H_2O]_m$.

$2H_2O]_m$ and $[Ni(RPOH)Cl \cdot 4H_2O]_m$ has been measured in the range from 74 to 294 K. The susceptibilities follow the Curie-Weiss relationship (Figure 3). The values of Θ measured from X'^{-1}_M *vs.* T plots are —11 and —3, respectively. The dependence of magnetic moments on temperature, when calculated from $\mu = \sqrt{X'_M (T—\Theta)}$, was rather low. For the Ni(II) complex it was negligible.

In summary, the analytical, magnetic and spectral data support the conclusion that the complexes $[M(RPPh)_3] [MCl_4] \cdot 4H_2O$ are monomeric complexes with the metal(II) ion in a more or less distorted octahedral and tetrahedral environment.

For $[Co(RPOH)Cl \cdot 2H_2O]_m$ a tetrahedral, and for $[Ni(RPOH)Cl \cdot 4H_2O]_m$ an octahedral surrounding of the metal ion has been proposed. Far IR data of these complexes are indicative for a dimeric or polymeric structure. Bridging through oxygen or chlorine atoms, for the cobalt and nickel complex respectively, is plausible. As the distances between the two metal ions in the complexes, if bridged by O or Cl atoms, can be quite large, a major contribution of a direct M—M interaction to the antiferromagnetism of the complexes is not likely, if the complexes are polymeric. Both complexes are amorphous and of low solubility in common solvents. Therefore X-ray structure analysis, as well as molecular weight measurement have not been determined. According to the data obtained dimeric or polymeric structures as given in Figure 4., are proposed.

Far IR and visible spectral data for $[Cu(RPOH)Cl]_m$ are indicative of tetragonal distorted octahedral geometry. As RPOH preferentially acts as a bidentate ligand[10] there is a great probability that this complex also has a polymeric structure.

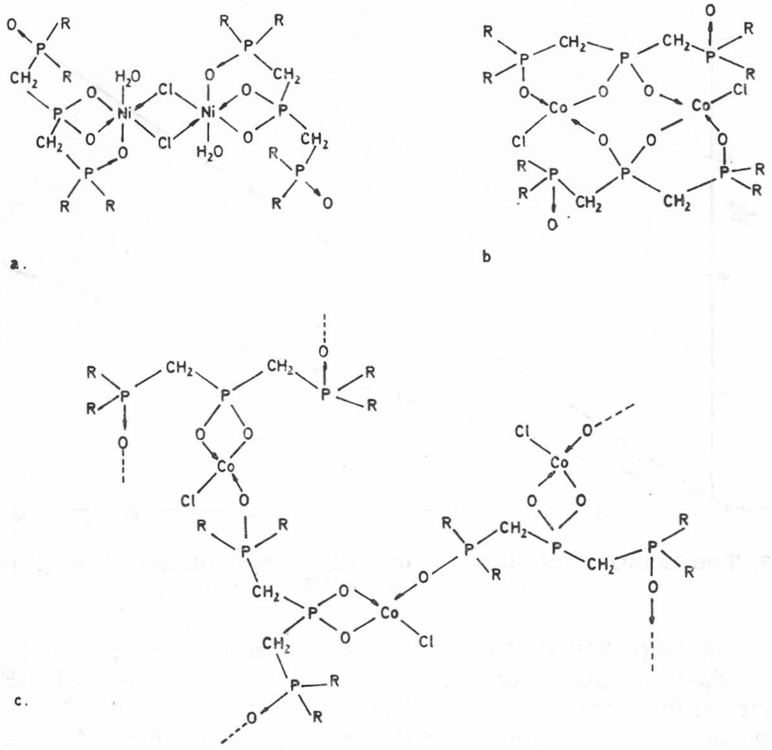


Figure 4. Predicted structures of the complexes of (a) $[Ni(RPOH)Cl \cdot 4H_2O]_2$; (b) $[Co(RPOH)Cl \cdot 2H_2O]_2$; (c) $[Co(RPOH)Cl \cdot 2H_2O]_m$.

EXPERIMENTAL

Materials

Analytical grade solvents and hydrated metal(II) chlorides (Merck p. a.) were used throughout the preparation. The ligands, bis[(diphenylphosphinyl)methyl]phenylphosphine oxide (RPPh) and bis[(diphenylphosphinyl)methyl]phosphinic acid (RPOH) were prepared by the method of Kabachnik et al.[36]

For conductivity measurements nitrobenzene was purified by the method of Taylor and Kraus.[37]

Physical Measurements

Infrared spectra in the 4000—200 cm^{-1} region were recorded on KBr-pellets and nujol mulls using a Perkin-Elmer Model 580 B spectrophotometer. Far IR samples were prepared as nujol mulls supported between rigid polyethylene plates.

Electronic spectra were obtained using a Carry Model 17 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method at 295 K using $CuSO_4 \cdot 5H_2O$ as calibrant. Diamagnetic corrections were calculated from Pascal's constants.

At multiple temperatures in the range 74—294 K the magnetic susceptibility of powdered samples of the complexes was measured using a Faraday balance.

Electrolytic conductance determinations were made on a Tacussel conductivity bridge, type Cd7, at 298 K.

The amount of water was determined by the Karl-Fischer method.

Preparation of Complexes

The complexes were prepared by direct interaction of the metal salts and ligands in the appropriate molar ratio in absolute ethanol or dichloromethane.

$Co(RPPh)Cl_2 \cdot 2H_2O$ By adding 0.238 g (1 mmol) $CoCl_2 \cdot 6H_2O$ dissolved in 3 ml of hot absolute ethanol to an ethanolic solution (5 ml) of 0.554 g (1 mmol) RPPh a blue crystalline precipitate was formed. After the mixture was allowed to stand for a short time the crystals were filtered off, washed with absolute ethanol and diethylether and then air-dried.

$[Co(RPPh)_3][CoCl_4] \cdot 4H_2O$ and $[Ni(RPPh)_3][NiCl_4] \cdot 4H_2O$ 0.238 g metal(II) chloride hexahydrates (1 mmol) were dissolved in abs. ethanol (3 ml) and added to a warm dichloromethane solution (8 ml) containing 0.831 g RPPh (1.5 mmol). The resulting solution was refluxed for 30 minutes. After cooling anhydrous diethylether was added. Blue and green precipitates were formed, respectively. These were filtered off, washed with diethylether and dried at room temperature.

$[Cu(RPPh)_3][CuCl_4] \cdot 4H_2O$ 0.171 g copper chloride dihydrate (1 mmol) dissolved in 3 ml of hot abs. ethanol was added to a warm solution of 0.554 g RPPh (1 mmol) in 5 ml of absolute ethanol. The solution was allowed to stand overnight and the yellow crystals were filtered off, washed with absolute ethanol and diethylether and then air-dried.

$[M(RPOH)Cl \cdot nH_2O]_m$; M = Co(II), Ni(II), Cu(II). To a warm solution of 0.494 g RPOH (1 mmol) in 25 ml of absolute ethanol was added 1 mmol of the appropriate metal(II) chloride dissolved in 3 ml of hot absolute ethanol. In all cases the solid complexes precipitated out almost immediately. The precipitate was filtered off, washed with abs. ethanol and diethylether and dried.

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SAŽETAK

Priprava i opis kompleksa kobalt(II)- nikal(II)- i bakar(II)-klorida s bis[(difenilfosfinil)metil]fenilfosfin oksidom i bis[(difenilfosfinil)metil]fosfinskom kiselinom

P. Bronzan-Planinić i H. Meider

Istraživan je niz kompleksnih spojeva kobalt(II)-, nikal(II)- i bakar(II)-klorida s tridentatnim organofosfornim spojevima bis[(difenilfosfinil)metil]fenilfosfin oksidom (RPPh) i bis[(difenilfosfinil)metil]fosfinskom kiselinom (RPOH). Izoliranim spojevima pripisane su slijedeće formule: $[M(RPPh)_3][MCl_4]\cdot 4H_2O$ i $[M(RPOH)Cl\cdot nH_2O]_m$ (M = = Co(II), Ni(II) ili Cu(II); n = 0 — 4, m = 1, 2 ili više).

Spojevi su karakterizirani na osnovi mjerenja magnetskih susceptibilnosti, molarne provodnosti te infracrvenih i elektronskih spektara.

Na temelju dobivenih podataka pretpostavljeno je da su spojevi s RPPh binuklearni, te da je metal u kompleksu okružen ligandima tvoreći oktaedar, a s atomima klora tetraedar.

U spojeva $[M(RPOH)Cl\cdot nH_2O]_m$ prevladava elektronski efekt metalnog iona. Za kompleks kobalta(II) pretpostavljeno je tetraedarsko, a za kompleks nikla(II) oktaedarsko okruženje. U kompleksu bakra(II) nalazi se simetrija izduženog oktaedra.