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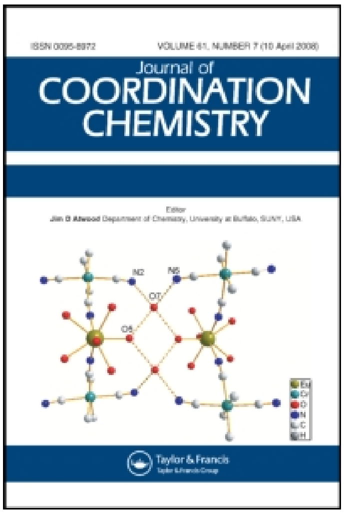

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Chromium(III), Cobalt(II), Nickel(II) and Copper(II) Complexes of (Dimethyl-Phosphinyl)Methanamine. Crystal Structure of *fac*-Tris{(Dimethyl-Phosphinyl)Methanamine-N, O}Nickel(II) Chloride Trihydrate

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CHROMIUM(III), COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES OF (DIMETHYLPHOSPHINYL)METHANAMINE. CRYSTAL STRUCTURE OF *fac*-TRIS{(DIMETHYLPHOSPHINYL)METHANAMINE-N, O}NICKEL(II) CHLORIDE TRIHYDRATE

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The complexes $CrL_3Cl_3.2H_2O$ (1), $CoL_3Cl_2.3H_2O$ (2), $CoL_3Br_2.H_2O$ (3), $NiL_3Cl_2.3H_2O$ (4) and $CuLCl_2$ (5), where L is (dimethylphosphinyl)methanamine, were synthesized and characterized by infrared and electronic spectra. The X-ray single crystal analysis of 4 (trigonal, space group $R\bar{3}c$, $a = 11.340(2)$, $c = 63.708(8)$ Å, $V = 7095(2)$ Å, $Z = 12$) revealed a structure containing tris-chelated *fac*-$[NiL_3]^{2+}$ cations in which L is coordinated *via* the amino nitrogen and phosphoryl oxygen atoms. The statistically disordered chloride ions and water molecules occupy voids between the cations. On the basis of spectral data, 1, 2 and 3 are formulated as consisting of pseudo-octahedral tris-chelate cations $[ML_3]^{n+}$ (n = 2 or 3) and non-coordinated halide ions and water molecules. A polymeric structure in which Cu(II) is surrounded by four bridging chlorides and two bridging L ligands is ascribed to 5.

Keywords: Chromium(III), cobalt(II), nickel(II), copper(II), (dimethylphosphinyl)methanamine, X-ray structure

INTRODUCTION

Aminosubstituted phosphine oxides are of interest as potential polydentate ligands possessing two types of donor atoms—the amino group nitrogen and oxygen from the phosphoryl group. They form transition metal complexes of various structures.[1-10] Recently[11] we described the synthesis, characterization and antitumor effect of platinum(II) and (IV) and palladium(II) complexes of 1,1'-(methylphosphinylidene)bis(methanamine),$CH_3P(O)(CH_2NH_2)_2$, and (dimethylphosphinyl) methanamine, $(CH_3)_2P(O)CH_2NH_2$ (L), in which these ligands act as nitrogen donors. The present work is an extension of the study on the coordination ability of L toward some 3d transition metals, for which coordination of the ligand through both the nitrogen and oxygen is expected. Especially, the feature that L melts at low temperatures (35–37°C) allowed us to attempt to prepare some of its complexes in the absence of solvent, by reacting metal salts with an excess of the molten ligand.

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Thus we expected to achieve a high value of ligand-to-metal ratio in the complexes obtained.

EXPERIMENTAL

The ligand L was prepared as described previously.[12] The metal salts and solvents were AR grade reagents.

Preparation of the Complexes

$CrL_3Cl_3.2H_2O$, $CoL_3Cl_3.3H_2O$, $CoL_3Br_2.H_2O$ and $NiL_3Cl_2.3H_2O$ were prepared by the following procedure. A tenfold excess of L (*ca* 1.5 g) was melted at 50–60°C under stirring with the corresponding anhydrous metal halide (0.2–0.3 g) until most of the salt reacted (*ca* 2 h for $CrCl_3$ and *ca* 20 min for the remaining salts). The complexes formed were then separated from unreacted ligand and metal salts. In the case of the Cr(III) complex, the reaction mixture was dissolved in a small portion of methanol and unreacted $CrCl_3$ was filtered off. The filtrate was stirred with hot toluene (*ca* 30 cm^3) to settle the complex as an oil. The solvent was decanted and the treatment of the crude complex with methanol and toluene was repeated three times. Finally the product was dried *in vacuo*. Yield: 45%. In the cases of Co(II) and Ni(II) complexes, the obtained melts were poured from the unreacted starting salts into hot toluene (*ca* 20 cm^3), stirred for some minutes and the toluene decanted. The purification procedure with toluene was repeated two to three times. The complexes were recrystallized from nitromethane and dried *in vacuo*. Yields: 40–48%.

$CuLCl_2$ was prepared by mixing solutions of stoichiometric amounts (*ca* 10^{-3} mol) of $CuCl_2$ and L in ethanol (*ca* 3 cm^3) at room temperature. The precipitate obtained was filtered, washed with ethanol and dried *in vacuo*. Yield: 90%.

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X-ray Crystal Structure Determination of $NiL_3Cl_2.3H_2O$

Crystal data

$C_9H_{36}Cl_2N_3NiO_6P_3$, $M_w = 504.94$, trigonal, space group $R\bar{3}c$ (No. 167), $a = 11.340(2)$, $c = 63.708(8)$ Å, $V = 7095(2)$ Å^3, $Z = 12$, $D_x = 1.418\ cm^{-3}$, $F(000) = 3192$, $\lambda(MoK\alpha) = 0.70930$, $\mu = 12.8\ cm^{-1}$, $T = 291$ K.

Crystals suitable for X-ray analysis were obtained from a saturated nitromethane solution of the complex upon slow evaporation at room temperature. A greenish-blue prismatically shaped crystal with approximate dimensions 0.3 × 0.3 × 0.6 mm was investigated on an Enraf Nonius CAD-4 diffractometer (graphite monochromator, MoKα radiation); $\omega/2\theta$ scan; speed 1 to 7 deg min^{-1}, width = $(0.8 + 0.4\tan\theta)°$; cell constants from least-squares refinement of 22 reflections with $18.0 < \theta < 20.0°$; 2919 reflections measured in range $\sin\theta/\lambda < 0.572$ (h: 0 to 13, k: 0 to 13, l: −73 to 73); 3 standard reflections monitored every 2.0 hours; intensity variation < 1.0%; no decay correction; Lorentz and polarization correction; no absorption correction; 1248 unique reflections with $R_{int} = 0.012$; structure solved by Patterson technique and refined by full-matrix least-squares on F; H-atoms in $[NiL_3]^{2+}$ were localised and refined with fixed B; final $R = 0.041$, $R_w = 0.061$ and $S = 2.185$ for 845 reflections with $I > 3\sigma(I)$; weights w defined as $4F_o^2/[\sigma(F_o)^2]^2$; max. shift/error = 0.049; max. and min. residual densities 0.50 and −0.43e. Å^{-3}; no correction for

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TABLE I
Elemental analyses and physical properties of the complexes.

Complex	Colour	M.p. (°C)	Elemental analyses (%)[a]				$\Lambda_m(\Omega^{-1}\ mol^{-1}\ cm^2)$[b]
			C	H	N	X	(c(mol dm^{-3} × 10^3))
$CrL_3Cl_3.2H_2O$	deep	218–	21.27	6.74	7.63	20.91	67.3 (0.97)
	green	222	(20.96)	(6.65)	(8.15)	(20.63)	
$CoL_3Cl_2.3H_2O$	pink	99–	21.64	6.92	8.19	13.54	25.6 (0.89)
		102[c]	(21.40)	(7.18)	(8.32)	(14.04)	
$CoL_3Br_2.H_2O$	pink	205–	19.45	6.11	8.26	28.63	66.0 (0.98)
		207[c]	(19.37)	(5.78)	(7.53)	(28.64)	
$NiL_3Cl_2.3H_2O$	greenish-	154–	21.96	7.60	8.03	14.58	43.8 (1.10)
	blue	155	(21.41)	(7.19)	(8.32)	(14.04)	
$CuLCl_2$	blue-	*ca* 200	15.44	3.86	5.77	29.04	31.0 (0.54)
	green	(dec.)	(14.92)	(4.17)	(5.80)	(29.36)	

[a] Calculated values in parentheses. [b] Molar conductivities measured in dimethylformamide ($CrL_3Cl_3.2H_2O$) and nitromethane (the remaining complexes).
[c] In the melt the colour changes to blue.

secondary extinction. Atomic scattering factors and anomalous-dispersion coefficients were as coded in the SDP/PDP V3.0 software. A PDP11/44 computer was used, for all calculations. Lists of anisotropic thermal parameters and observed and calculated structure factors have been deposited with the Editor.

Analyses and Physical Measurements

Elemental analyses for C, H, N and halogen were performed according to standard microanalytical procedures. Melting points were measured on a Boëtius apparatus or in a sealed capillary ($CrL_3Cl_3.2H_2O$) and are uncorrected. Conductivities were determined at 25°C in dry, freshly distilled nitromethane or dimethylformamide using a Radiometer CDM83 conductometer. Infrared spectra were recorded on a Specord M80 spectrophotometer (4000–200 cm^{-1}) in nujol mulls and on a Bruker IFS-113V instrument (450–100 cm^{-1}) in polyethylene discs. Diffuse reflectance electronic spectra were recorded on a Perkin-Elmer 330 apparatus using $BaSO_4$ as reference. Solution electronic spectra were measured on a Beckman 5270 spectrophotometer. The sampling of the hygroscopic compounds L and $CrL_3Cl_3.2H_2O$ was carried out in a dry box.

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RESULTS AND DISCUSSION

In Table I the analytical data and some physical properties of the new complexes are summarized. All the complexes synthesized in a melt have a ligand-to-metal ratio of 3:1 and they contain water. The water was obviously introduced into the complexes during the preparations due to the high hygroscopicity of L. The complex prepared in solution is of the 1:1 type and does not contain water. With the exception of $CrL_3Cl_3.2H_2O$, the complexes do not appear to be hygroscopic. They are soluble in water, alcohols, dimethylformamide and nitromethane (except $CrL_3Cl_3.2H_2O$). Crystals suitable for X-ray structure analysis were only obtained for $NiL_3Cl_2.3H_2O$. Attempts to grow crystals of the remaining compounds were unsuccessful.

TABLE II

Positional and equivalent isotropic thermal parameters for $NiL_3Cl_2.3H_2O$.[a]

Atom	x/a	y/b	z/c	$B_{eq}(Å^2)$
Ni	0.0000	0.0000	0.12383(2)	2.48(2)
P	0.2757(1)	0.0420(1)	0.13640(2)	2.77(3)
O	0.1777(3)	0.0893(3)	0.14218(4)	3.08(8)
N	0.0977(4)	−0.0833(4)	0.10580(6)	3.2(1)
C(1)	0.2469(5)	−0.0087(5)	0.10917(8)	3.4(1)
C(2)	0.2509(5)	−0.1009(6)	0.15143(9)	4.2(2)
C(3)	0.4502(5)	0.1697(5)	0.13905(9)	4.3(2)
Cl(1)	0.1129(3)	0.3914(3)	0.22344(6)	6.9(1)
Cl(2)	0.0000	0.0000	0.05991(8)	5.6(1)
O(1W)	0.0241(9)	0.1735(7)	0.2468(2)	7.4(2)
O(2W)	0.091(1)	0.3794(9)	0.2111(1)	7.9(3)

[a] Estimated standard deviations in parentheses. B values for the anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3\ [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

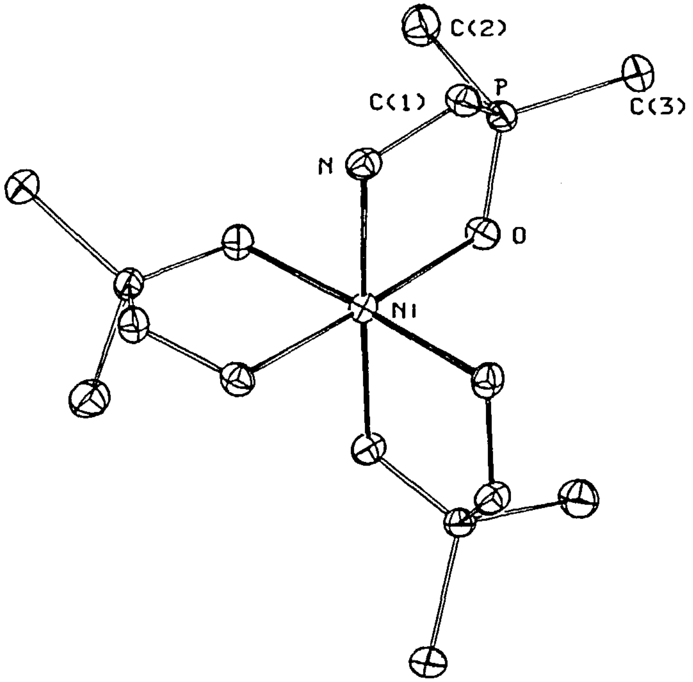

FIGURE 1 View of the $[NiL_3]^{2+}$ cation along the three-fold axis showing 20% probability ellipsoids and the atomic labelling scheme.

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Structure of $NiL_3Cl_2.3H_2O$

The positional and equivalent isotropic thermal parameters for the atoms are given in Table II. The crystal structure of the compound consists of tris-chelated $[NiL_3]^{2+}$ cations, and statistically disordered chloride anions and water molecules are distributed over the voids between the bulk complex species. The structure of the cation $[NiL_3]^{2+}$ with the atomic numbering scheme is presented in Figure 1, and selected interatomic distances and angles are listed in Table III. The nickel(II) ion is placed in special position of the $R\bar{3}c$ space group on the threefold axis (*c* in Wyckoff notation, 1/3 of the general position) and is surrounded trigonal-antiprismatically by the nitrogen and oxygen atoms of the three L ligands. This coordination polyhedron differs from an ideal *fac*-octahedron only slightly; values of Ni-O and Ni-N bond lengths are 2.100(2) and 2.118(3) Å, respectively, the X-Ni-X′ (X, X′ = O, N) angles lie within 85.8(1)-93.4(1)°, and the polyhedron edge lengths are for $O \ldots O^i$ (i: $-y$, $x-y$, z) 3.022(4), $N \ldots N^i$ 3.082(6) and $O \ldots N$, $O \ldots N^i$ 2.872(4), 2.951(4) Å, respectively. The twist angle[13] between the triangular O_3 and N_3 faces is 57.5°. The ligand L forms a non-planar five-membered chelate ring which conformation is characterized by the puckering parameters $q_2 = 0.389$Å, $\varphi_2 = 102.09°$ [14]. Atoms P and C(1) deviate from the Ni, O, N plane by −0.172(1) and 0.451(5) Å, respectively.

The chloride ions and water molecules are distributed over three different voids. The first void, in a general position of the space group, is shared (50%) by Cl(1) and O(2W) (Cl(1)...O(2W) 0.814(7) Å). These two atoms approach the H(2) amino hydrogen at distances of 2.56(5) and 2.40(5) Å, respectively; the angles

N–H(2)...Cl(1)^{iii}, N–H(2)...O(2W)^{iii} (*iii*: $-1/3 + y$, $-2/3 + y - x$, $1/3 - z$) are 128(4), 144(4); respectively. The second void on the threefold axis (Wyckoff *c* position) is 50% occupied by Cl(2). Thus the Cl : Ni ratio is, as follows from the charge balance, 2 : 1. The distance from Cl(2) to the second amino hydrogen atom H(1) is 2.70(5) Å, and the N–H(1)...Cl(2) angle is 151(5)°. The third void, disposed close to the two-fold axis position, is again by 50% occupied by O(1W) (O(1W)...O(1W) ($-x$, $y - x$, $-1/2 - z$) 0.62(3) Å). The three water molecules found in the course of the crystal structure analysis are in accordance with the results of elemental analysis which is consistent with a Ni : H_2O ratio of 1 : 3. The interatomic distance O(1W)...O(1W) (y, x, $-1/2 - z$) of 2.96(4) Å corresponds to a typical O...H–O hydrogen bond.

TABLE III

Selected bond lengths (Å) and angles (°) for the cation $[NiL_3]^{2+}$.[a]

Bond lengths			
Ni–O	2.100(2)	P–C(1)	1.805(4)
Ni–N	2.118(3)	P–C(2)	1.780(5)
P–O	1.502(3)	P–C(3)	1.781(4)
		N–C(1)	1.481(6)
Bond angles			
O–Ni–O^{i}	92.0(1)	O–P–C(1)	107.5(2)
O–Ni–N	85.8(1)	O–P–C(2)	112.6(2)
O–Ni–N^{i}	88.8(1)	O–P–C(3)	113.9(2)
O–Ni–N^{ii}	177.7(1)	C(1)–P–C(2)	107.8(2)
N–Ni–N^{i}	93.4(1)	C(1)–P–C(3)	107.5(2)
Ni–O–P	113.2(1)	C(2)–P–C(3)	107.1(2)
Ni–N–C(1)	111.7(2)	P–C(1)–N	107.1(3)
Torsion angles			
N–Ni–O–P	−7.2(2)		
O–Ni–N–C(1)	−19.1(3)		
C(1)–P–O–Ni	26.5(3)		
O–P–C(1)–N	−41.0(4)		
Ni–N–C(1)–P	35.8(4)		

[a] Estimated standard deviations in parentheses. Symmetry codes: *i*) $-y$, $x - y$, z; *ii*) $y - x$, $-x$, z.

Infrared Spectra

Characteristic infrared absorptions of the ligand L and its complexes are given in Table IV. Since the structure of $NiL_3Cl_2.3H_2O$ was determined, we will begin discussion of the infrared spectra with this complex. In $NiL_3Cl_2.H_2O$ the three L molecules were found to be coordinated to the metal ion *via* both the amino and phosphoryl groups. Therefore a low frequency shift of N–H and P=O stretching bands as compared to the free ligand should take place.[15,16] This is indeed observed in the spectrum of $NiL_3Cl_2.3H_2O$. The ν(P=O) band is split into a doublet. Similar splitting has been observed for a number of phosphoryl complexes.[17–19] For the present case this seems most likely to be caused by coupling between the P=O vibrations. The bands due to O–H stretches of lattice water molecules as well as those

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of H–N–H and H–O–H bending vibrations were also observed. Since L itself exibits a number of bands in the far infrared region, the assignment of metal–ligand vibrations is complicated (see below). No extra bands assignable to Ni–Cl stretches were observed, in accordance with the X-ray structure data.

TABLE IV
Selected infrared bands (cm^{-1}) for L and its complexes.

Compound	ν(OH)	ν(NH)	δ(HOH) δ(HNH)	ν(PO)	Far i.r. bands (550–200 cm^{-1})
L		3336s 3285s 3200s	1616m	1165vs 1130s	440s,br, 400s, 358sh, 348s, 306w, 286m,br, 258m, 234sh
$CrL_3Cl_3.2H_2O$	3400sh	3200sh 3070s	1605m,br	1130vs,br 1076vs	538s,br, 476s, 390sh, 360s,br, 318w,br, 290w,br, 258m, 250m, 242m, 232m
$CoL_3Cl_2.3H_2O$	3450s	3275s,br 3160s	1648m 1612m	1128vs 1060vs	470sh, 460s, 400sh, 383m, 360s, 303w, 278m,br, 247w,br, 220w,br
$CoL_3Br_2.H_2O$	3465s	3320s,br 3152s	1640m 1608m	1128vs 1064vs	468sh, 460s, 400sh, 385m, 360s, 303w, 276m,br, 252sh, 223m,br
$NiL_3Cl_2.3H_2O$	3450s	3275s,br 3175s	1655m 1615m	1135vs 1075vs	468s,br, 408m, 388m, 362s, 310w, 288m, 270sh 232m,br
$CuLCl_2$		3265s 3225s 3130m	1578m	1096vs	508m, 466s, 400w, 374m, 348m, 308s, 285m, 268m, 243m

The infrared spectra of the remaining complexes, except for $CuLCl_2$, closely resemble the spectrum of $NiL_3Cl_2.3H_2O$, indicating coordination of L through both the amino and phosphoryl groups and presence of water. The phosphoryl stretching bands are again split. The metal–halogen stretches are expected in the range 400–200 and 300–200 cm^{-1} (or lower) for chloro and bromo complexes, respectively.[15] For $CrL_3Cl_3.2H_2O$, $CoL_3Cl_2.3H_2O$ and $CoL_3Br_2.H_2O$, no bands in this interval were observed. The spectra of the latter two complexes were also recorded in the region below 200 cm^{-1} and compared to each other. The close similarity between them remains, indicating absence of bands assignable to Co–Br vibrations.

The spectrum of $CuLCl_2$ also bears evidence of coordination of L *via* both the amino and phosphoryl functions. The ν(P=O) band in this case is not split. In accordance with the elemental analysis, bands assignable to ν(O–H) and δ(H–O–H) are absent. The spectrum of this complex in the far infrared region is similar to those of the remaining complexes, with the exception that a strong band at 308 cm^{-1} is observed. We ascribe this band to Cu–Cl stretching. The reasons for such an assignment are the following. Although the spectra of L and the remaining complexes do exhibit bands in the interval 303–318 cm^{-1}, these absorptions are weak, in contrast to the strong band in the spectrum of $CuLCl_2$. The stoichiometry of the complex and its electronic spectrum, which suggests hexacoordinated Cu(II) (see below), requires the presence of bridging chloride ligands. It is known that compounds of the type CuY_2Cl_2 (Y_2 stands for two monodentate or one bidentate ligand) usually give a strong single absorption at about 300 cm^{-1} which is ascribed to

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the short Cu–Cl bond in a polymeric distorted octahedral structure with bridging chlorides.[20,21] A similar structure can thus be suggested for $CuLCl_2$.

In the spectra of the complexes, bands were observed in the interval 538–468 cm^{-1}, which are not observed in the free ligand ($NiL_3Cl_2.3H_2O$ exhibits a single but broad absorption at 468 cm^{-1}). In the same region metal–nitrogen stretches for some complexes of aminosubstituted phosphine oxides[9] and diamines[22,23] were reported. Thus, the bands mentioned can tentatively be ascribed to ν(M–N) of the coordinated ligand. Metal–oxygen stretches of the coordinated phosphoryl groups are expected in the range 450–350 cm^{-1}.[24] The assignment of these vibrations is often complicated due to coupling between them and P=O bending modes,[24,25] or because of their low intensity.[19] For the complexes reported here we could not identify the metal–oxygen stretches.

Electronic Spectra

Table V contains diffuse reflectance spectral data for the complexes and calculated ligand-field parameters. Although the true local symmetry of the chromophore in $NiL_3Cl_2.3H_2O$ is C_3, the spectrum of this complex corresponds to octahedrally coordinated Ni(II).[26] No band splitting due to lowering of the symmetry from O_h was observed. This was not surprising since the X-ray structure showed only slight deviations from ideal octahedral geometry. The spectra of $CrL_3Cl_3.2H_2O$, $CoL_3Cl_2.3H_2O$ and $CoL_3Br_2.H_2O$ are also in acccordance with octahedral metal ions.[27,28] The spectra of $CoL_3Cl_2.3H_2O$ and $CoL_3Br_2.H_2O$ are almost identical, thus suggesting the presence of the same chromophore in both compounds. The values of the splitting parameter Δ and the Racah parameter β for the complexes fall in the usual range for octahedral Cr(III),[27] Co(II)[28] and Ni(II)[26] complexes. The values of the Jørgensen spectrochemical parameter f[27] are similar as expected for one and the same coordination sphere. The averaged value of $f = 1.02$ indicates that L is a ligand of moderate strength, occupying approximately the same position in the spectrochemical series as NCS^-.[27]

TABLE V

Electronic spectral data and ligand-field parameters for the complexes of L.[a]

Complex	Band maxima (cm^{-1})	and assignments	Δ(cm^{-1})	B(cm^{-1})	β	f
$CrL_3Cl_3.2H_2O$	$^4T_{1g}(F) \leftarrow {}^4A_{2g}$ 24100 $^2T_{2g}, {}^2E_g(G) \leftarrow {}^4A_{2g}$ 14500sh	$^4T_{2g} \leftarrow {}^4A_{2g}$ 17250	17250	683	0.74	0.99
$CoL_3Cl_2.3H_2O$, $CoL_3Br_2.H_2O$	$^4T_{1g}(P) \leftarrow {}^4T_{1g}$ 19700 $^4T_{2g} \leftarrow {}^4T_{1g}$ 8330	$^4A_{2g} \leftarrow {}^4T_{1g}$ 16100sh	9090	829	0.85	1.01
$NiL_3Cl_2.3H_2O$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$ 26200 $^1E_g(D) \leftarrow {}^3A_{2g}$ 13200sh	$^3T_{1g} \leftarrow {}^3A_{2g}$ 15500 $^3T_{2g} \leftarrow {}^3A_{2g}$ 9250	9250	911	0.88	1.06
$CuLCl_2$	12500br, asymm.					

[a] Δ-splitting parameter; B-Racah parameter; $\beta = B/B_{free\ ion}$-reduced Racah parameter; $f = \Delta/g_{metal\ ion}$-spectrochemical parameter of the ligand.

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In the spectrum of $CuLCl_2$ a broad and asymmetric band was observed with a maximum at *ca* 12500 cm^{-1}. The position and shape of this band suggests hexacoordinated Cu(II), probably in a tetragonally distorted environment.[24,25,27] Since this band is not well resolved, the assignment of its components is complicated.

Differences were observed between the solution behaviour of the complexes as indicated by their electronic absorption spectra. The spectra of $CrL_3Cl_3.2H_2O$ in dimethylformamide and of $NiL_3Cl_2.3H_2O$ in nitromethane do not differ significantly from the corresponding solid-state spectra. However, $CoL_3Cl_2.3H_2O$ forms a blue solution in nitromethane which exhibits two intense complex bands at 15000 and 6600 cm^{-1} and two weak absorptions at 19600 and *ca* 8300 cm^{-1}. The positions of the latter two bands are practically unchanged with respect to the solid-state spectrum, while the positions of the former two are typical for the tetrahedral Co(II) complexes.[27] It is obvious that, upon dissolution, this complex partially dissociates into tetracoordinated species. Such behaviour is not uncommon among Co(II) complexes of amino-substituted phosphine oxides.[3] The room temperature solubility of $CoL_3Br_2.H_2O$ in nitromethane is insufficient to obtain an absorption spectrum. However, upon heating a blue solution is again produced. The yellow solution formed by $CuLCl_2$ in nitromethane shows an intense band at 21600 cm^{-1} and a broad absorption at about 11500 cm^{-1}. Similar spectra have been reported for the two isomers (yellow and orange in colour) of $Cu(Ph_3PO)_2Cl_2$, both being found to be pseudo-tetrahedral.[29,30] It seems likely that dissolution leads to destruction of the polymeric structure of $CuLCl_2$ and to the formation of tetracoordinated species.

The results suggest for the complexes $CrL_3Cl_3.2H_2O$, $CoL_3Cl_2.3H_2O$ and $CoL_3Br_2.H_2O$ a structure similar to that of $NiL_3Cl_2.3H_2O$. They can be formulated as consisting of pseudo-octahedral tris-chelate $[ML_3]^{n+}$ (n = 2 or 3) cations and noncoordinated halide anions and water molecules. The molar conductivity values for these complexes, including $NiL_3Cl_2.3H_2O$ (Table I) were, however, rather lower than expected for the corresponding electrolyte types.[31] This feature is not unequivocally explicable; it can be supposed that in solution ion association takes place due to hydrogen bonding between the amino groups and the halide ions, similar to the case with the solid-state structure of $NiL_3Cl_2.3H_2O$. A polymeric distorted octahedral structure involving Cu(II) ions surrounded by four bridging chlorides and two bridging L ligands can be proposed for $CuLCl_2$.

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