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Pyrazoles and Imidazoles as Ligands. II. Coordination Compounds of N-methyl Imidazole with Metal Perchlorates and Tetrafluoroborates

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A number of new coordination compounds containing N-*methyl imidazole (NMIz) as a ligand is reported. The compounds have the general formula* M(NMIz)$_m$(anion)$_n$, *in which* $M = Ag^I$ *or one of the divalent metal ions Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd;* $m = 2,4$ *or 6, the anions are* ClO_4^- *or* BF_4^-, *whereas* $n = 1$ *or 2.*

The compounds are prepared from the (hydrated) metal salts and the proper ligand in ethanol solution. Characterization and identification of the compounds occurred with the aid of chemical analyses, X-ray powder diagrams, ligand-field spectra, infrared and ramanspectra, magnetic susceptibility measurements and paramagnetic resonance spectra. Several compounds of the same stoichiometry were found to be mutually isomorphous.

The ligand NMIz is believed to be coordinated via *the pyridine nitrogen of the molecule, to all metal ions. Magnetic data, such as the magnetic moments, g-values, nuclear hyperfine splittings, zero-field splittings, all agree with the proposed stoichiometry. Ligand-field parameters are determined for the octahedral ions* $M(NMIz)_6^{2+}$ *with* $M = Fe$, *Co, Ni, and for the square-planar* $Cu(NMIz)_4^{2+}$, *and compared with* $M(imidazole)_n^{2+}$ *ions. Far-infrared and raman spectra indicate M—N stretching frequencies in the 350-150* cm^{-1} *range, as found for many other nitrogen-donor ligands.*

Introduction

The first part in this series[1] described the ligand properties of both pyrazole and imidazole. These ligands were found to coordinate to metal ions *via* the pyridine nitrogen rather than the pyrrole nitrogen, yielding hexasolvates for most metal(II) prchlorates and tetrafluoroborates.

In order to see whether or not methyl substituted ligands behave similarly, and to investigate the influence of methylation upon the ligand-field spectra of the compounds with the transition-metal ions, a number of compounds containing coordinated N-methyl imidazole (NMIz) were studied. Their preparation properties and structures will be subjects of the present paper.

Only a few coordination compounds containing NMIz have been reported in the literature. Very recently, Perchard and Novak[2] described $ZnCl_2(NMIz)_2$, $CuCl_2(NMIz)_2$, and $AgNO_3(NMIz)_2$, and discussed their infrared spectra with respect to the uncoordinated ligand.[3]

Experimental Section

Starting Materials. *N*-methyl imidazole (Aldrich) was used without purification. Metal perchlorates and tetrafluoroborates were commercially available (in most cases as the hydrates), or were prepared from the metal hydroxydes or carbonates and either perchloric acid or hydrofluoboric acid

Preparation of the Solvates. All hexasolvates with NMIz were prepared as described for the Ni^{II} compound. Hexakis(*N*-methylimidazole) nickel^{II} perchlorate was prepared as follows: to a solution of 1.05 g of $Ni(H_2O)_6(ClO_4)_2$ (3 mmoles) in 10 ml of ethanol and 2 ml of triethyl orthoformate (for dehydration[4]), a solution of 1.65 g of NMIz (20 mmoles) in 20 ml of ethanol was added. Violet crystals immediately separated, which were washed with ethanol and after that three times with dry diethyl ether. Finally the crystals were dried *in vacuo*. The tetrasolvates were prepared in the same way, but using only 11 mmoles of NMIz in 10 ml of ethanol. $Ag(NMIz)_2ClO_4$ was synthesized in a more concentrated alcoholic solution, using 7 mmoles of NMIz to 3 mmoles of $AgClO_4$.

Analyses. Metal^{II} determinations were carried out by complexometric titrations. Carbon, hydrogen and nitrogen were determined by the micro-analytical department of the Organic Chemistry Institute TNO, Croesestraat 79, Utrecht.

Infrared Spectra. These spectra were recorded on a Hitachi EPI-G2 (4000-600 cm^{-1}), on a Hitachi EPI-L (700-200 cm^{-1}), and on a Perkin Elmer 301 spectrophotometer (350-150 cm^{-1}) as nujol mulls sandwiched between sodium chloride (down to 700 cm^{-1}) or polythene windows (below 700 cm^{-1}).

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Raman Spectra. Laser-raman spectra were measured on a Cary 81 instrument furnished with a Helium-Neon gas laser (6458 Å) using 50 mW power.

Ligand-field Spectra. Diffuse reflectance spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer, equipped with the standard reflectance attachment. The spectra were measured by the double-beam technique, with magnesium oxide as a reference. The ligand-field parameters were calculated using the weak-field formalism. Procedures for calculation of these parameters from the spectral data are given elsewhere.[5,6]

X-ray Powder Diagrams. These diagrams were obtained with a Guinier-de Wolff type powder camera using Cu-Kα radiation. The samples were mulled with vaseline and protected from the atmosphere between two sheets of adhesive tape.

Magnetic Measurements. Magnetic susceptibility measurements were carried out on a Gouy balance equipped with a temperature controller. As a calibrant $HgCo(CNS)_4$ was used.[7] Magnetic moments were calculated with the relation $\mu = \sqrt{8.T.\chi_{corr.}}$, in which $\chi_{corr.} = \chi_{mol.} - \chi_{dia.} - \chi_{TIP}$.

Paramagnetic Resonance Spectra. Measurements on powdered samples were performed on a Varian 4502 apparatus, furnished with a Varian 4531 multipurpose cavity, employing 100 kc/s field modulation. The X-band frequency was measured with a Hewlet-Packard 5245L electronic counter and a 2590A microwave frequency converter; Q-band frequency measurement occurred with the reference cavity placed in a 35 GHz microwave bridge. The magnetic field was calibrated with a Varian F8A fluxmeter, furnished with a proton probe. The spectra were run as the first derivative of the absorption line.

Results and Discussion

General. In Table I a number of coordination compounds containing *N*-methylimidazole is reported together with analytical results, colours and melting points. Further in this Table the X-ray types for the several compounds are indicated with the simbols A, B, C.

The division into these groups was made according to the X-ray powder diagrams of the compounds, which were very similar in *d*-values (Å) and intensities for members of the same group. The differences in line patterns for the groups A—compounds of formula $M(NMIz)_6(ClO_4)_2$—and A′—compounds of formula $M(NMIz)_6(BF_4)_2$—are only very small, and were not found for the perchlorate and tetrafluoroborate compounds of Cu^{II} and Zn^{II}, (of types B and C respectively).

These similarities in X-ray powder patterns strongly suggest isomorphism between the several compounds of the same group. in accordance with the observed stoichiometry of the solvates.

The occurrence of two kinds of compounds with $Zn(ClO_4)_2$ and $Zn(BF_4)_2$, *viz.* hexa- and tetrakis solvates, is rather surprising since most nitrogen-donor ligands yield either hexakis or tetrakis solvates with Zn^{II} salts.[1,8,9]

Most of the compounds reported in Table I are quite stable against moist air, although the Mg and Ca compounds showed slightly hygroscopic properties.

Ligand-field Spectra. Since the stoichiometry of the compounds reported in Table I suggests octahedral symmetry for the metal ions, ligand-field spectra for the transition-metal compounds were recorded, to see whether or not the band positions agreed with octahedral symmetry of M^{2+}.

In Table II absorption maxima and calculated Dq and B values are listed for the compounds of Fe, Co, Ni and Cu. Indeed the absorption bands could be assigned to the usual transitions found in octahedral solvates of Fe, Co and Ni, and tetragonal Cu^{II} solvates.[5,6,10,11]

The observed values for Dq for the several solvates are rather high compared with other ligands, but all fall in the usual range for nitrogen-donor ligands.[1,5,6] Compared with imidazole[1] NMIz is a markedly stronger ligand, as is easily seen by comparison of Dq values. For instance Dq(Fe) is 1140 cm^{-1} for imidazole (Iz) and 1150 cm^{-1} for NMIz; Dq(Co) is 1050 cm^{-1} for Iz and 1065 for NMIz; Dq(Ni) is 1065 for Iz and 1085 cm^{-1} for NMIz. The higher Dq values for the NMIz solvates must be due to the methyl group, and can be understood by considering this methyl group as an electron donating group. The same (small) effect was found in the pKa (base) of both ligands, that are 6.95 for Iz and 7.10 for NMIz.[12]

Magnetic measurements. Further information about the stereometry and the kind of bonding of NMIZ-coordinated transition-metal ions has been obtained with the aid of paramagnetic susceptibility and resonance measurements. The results of these investigations are summarized in Table III.

As can be seen from Table III the magnetic moments all fall in the usual range for octahedrally (or tetragonal for Cu^{2+}) coordinated metal(II) ions. The deviations of μ and g from the spin-only values for the Cu and Ni compounds are rather small, and are caused by a large Dq value and a small value of $|\lambda|$, the spin-orbit coupling constant. These deviations from the spin-only values are determined by the factors: $(1\text{-}2\lambda/10Dq)$ for Cu^{2+}, and $(1\text{-}4\lambda/10Dq)$ for Ni^{2+}.[11]

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Table I. Metal solvates of *N*-methyl imidazole; analyses, colours, X-ray types and melting points

Compound	% Metal fnd.	% Metal calc.	% Carbon fnd.	% Carbon calc.	% Hydrogen fnd.	% Hydrogen calc.	% Nitrogen fnd.	% Nitrogen calc.	Colour	X-ray type	Melting point
$Mn(NMIz)_6(ClO_4)_2$	7.50	7.35	38.4	38.6	4.98	4.83	22.5	22.5	white	A	280-281
$Mn(NMIz)_6(BF_4)_2$	7.71	7.61	39.6	39.9	4.95	4.98	23.1	23.3	cream	A'	241-242
$Fe(NMIz)_6(ClO_4)_2$	7.51	7.47	38.8	38.6	4.88	4.83	21.4	22.5	yellow	A	232 d.
$Co(NMIz)_6(ClO_4)_2$	7.82	7.86	37.9	38.4	4.80	4.80	21.7	22.4	orange	A	258 d.
$Co(NMIz)_6(BF_4)_2$	8.06	8.13	39.7	39.7	5.31	4.96	23.4	23.2	orange	A'	230 d.
$Ni(NMIz)_6(ClO_4)_2$	7.90	7.83	38.5	38.4	4.91	4.80	22.0	22.4	violet	A	293 d.
$Ni(NMIz)_6(BF_4)_2$	8.12	8.10	38.1	39.7	4.98	4.98	22.8	23.2	violet	A'	280 d.
$Cu(NMIz)_4(ClO_4)_2$	10.8	10.8	32.4	32.4	4.26	4.05	18.9	18.8	purple	B	257 d.
$Cu(NMIz)_4(BF_4)_2$	11.2	11.2	34.3	34.0	4.50	4.25	19.8	19.8	purple	B	236 d.
$Zn(NMIz)_4(ClO_4)_2$	11.1	11.0	32.5	32.4	4.26	4.05	18.4	18.7	white	C	172-174
$Zn(NMIz)_4(ClO_4)_2$	11.4	11.5	34.0	33.9	4.34	4.24	19.8	19.7	white	C	141-143
$Zn(NMIz)_6(ClO_4)_2$	8.69	8.64	38.1	38.1	4.87	4.77	22.0	22.2	white	A	177-178
$Zn(NMIz)_6(BF_4)_2$	8.93	8.98	38.8	39.4	4.84	4.93	22.3	22.9	white	A'	157-159
$Cd(NMIz)_6(ClO_4)_2$	14.2	14.0	36.0	35.8	4.78	4.48	20.6	20.9	white	A	263-265
$Cd(NMIz)_6(BF_4)_2$	14.5	14.4	37.1	37.0	4.49	4.63	21.9	21.6	white	A'	245-246
$Ag(NMIz)_2ClO_4$	—	—	26.1	25.9	3.34	3.23	15.0	15.1	cream	—	108-110
$Mg(NMIz)_6(ClO_4)_2$	3.43	3.39	39.3	40.2	5.34	5.03	21.9	23.4	white	A	289-290
$Ca(NMIz)_6(ClO_4)_2$	5.46	5.46	39.1	39.4	5.28	4.93	22.1	22.9	white	—	203-204

Table II. Diffuse reflectance spectra of NMIz solvates. Assignments and calculations according to references 5, 6 and 11

Compound	Band maxima (kK) and assignments				Dq(cm^{-1})	B(cm^{-1})
		$^5E_g \leftarrow {}^5T_{2g}$				
$Fe(NMIz)_6(ClO_4)_2$		11.5	10.0 sh		1150	—
	$^4T_{2g} \leftarrow {}^4T_{1g}$ (F)	$^4A_{2g}$, $^4T_{1g}$ (P),		$^2P \leftarrow {}^4T_{1g}$ (F)		
$Co(NMIz)_6(ClO_4)_2$	9.80	19.1 sh		20.8	1070	800
$Co(NMIz)_6(BF_4)_2$	9.75	19.2 sh		20.8	1065	800
	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^1E_g \leftarrow {}^3A_{2g}$	$^3T_{1g}$ (F)$\leftarrow {}^3A_{2g}$	$^3T_{1g}$ (P)$\leftarrow {}^3A_{2g}$		
$Ni(NMIz)_6(ClO_4)_2$	10.85	13.3 sh	17.55	28.2	1085	880
$Ni(NMIz)_6(BF_4)_2$	10.80	13.3 sh	17.50	28.1	1080	880
		^2E_g, $^2B_{2g} \leftarrow {}^2B_{1g}$				
$Cu(NMIz)_4(ClO_4)_2$		18.0			1800	—
$Cu(NMIz)_4(BF_4)_2$		18.0			1800	—

Table III. Magnetic data for solid solvates with N-methyl imidazole. Unless otherwise indicated measurements are at 293° K.

Compound	$\chi_{mol.}$ cgs. 10^6	$\chi_{corr.}$ [a] cgs. 10^6	μ (BM)	general μ range [b]	g value	Further parameters [c]	EPR region
$Mn(NMIz)_6(ClO_4)_2$	14400	14780	5.90	5.8—6.1	2.01 ± 0.01	—	X
Mn^{2+} in $Zn(NMIz)_6(ClO_4)_2$	—	—	—		2.00 ± 0.005	$A = 89 \pm 1$ G	X, Q
$Fe(NMIz)_6(ClO_4)_2$	13580	13960	5.72	5.2—5.8	—	—	—
$Co(NMIz)_6(ClO_4)_2$	10460	10840	5.04	4.6—5.4	—	—	—
Idem at 213° K.	14110	14490	4.97		—	—	—
Idem at 153° K.	18800	19180	4.87		—	—	—
Idem at 103° K.	25600	25980	4.64		—	—	—
$Ni(NMIz)_6(BF_4)_2$	—	—	—		2.17 ± 0.01	D=0.85 cm^{-1}	Q
$Ni(NMIz)_6(ClO_4)_2$	3740	3930	3.05	2.8—3.4	2.18 ± 0.01	D=0.91 cm^{-1}	Q
Ni^{2+} in $Zn(NMIz)_6(ClO_4)_2$	—	—	—		2.18 ± 0.01	D=0.91 cm^{-1}	Q
$Cu(NMIz)_4(ClO_4)_2$	1178	1405	1.82	1.7—2.0	2.06 [d]	—	X

[a] The diamagnetic correction was taken to be -380×10^{-6} units for all compounds, except for the Cu compounds for which a value of -285×10^{-6} units was taken; further TIP corrections were made for the Ni^{II} and Cu^{II} solvates, of 190×10^{-6} and 58×10^{-6} cgs units respectively. [b] According to reference 13. [c] A is taken to be the nuclear hyperfine splitting, whereas D is the zero-field splitting.[14] [d] Measured at the band maximum.

Substituting the observed g and μ values from Table III in these equations and using the Dq values from Table II, the λ-values can be calculated. Values of 330-460 cm^{-1} are found for λ_{Cu}, and of 215-245 cm^{-1} for λ_{Ni}. Compared to the free-ion $|\lambda|$-values (being 624 cm^{-1} for Cu^{II} and 315 cm^{-1} for Ni^{II}), these $|\lambda|$-values are notably reduced. However, these reductions are quite normal for strongly coordinating ligands[11] as NMIz is supposed to be, and are indicative for covalency in the metal-ligand bond.[15]

Similar indications for covalency can not be determined from g and μ values for the Mn, Fe and Co solvates, because the deviations from the spin-only values are theoretically less simple.[11] However, the nuclear hyperfine splitting constant (A) in Mn^2-doped $Zn(NMIz)_6(ClO_4)_2$, which was found to be 89 Gauss appeared to rather low compared with other $Mn(L)_6^{2+}$ ions, and must be due to increased covalency in the Mn-ligand bond. It is generally accepted that the lower the value of A, the more covalency must be present in the metal-ligand bond,[16,17] with an even linear dependence in the case of closely resembling compounds.[17] Some typical A values for octahedral Mn^{2+} solvates of formula $Mn(L)_6(ClO_4)_2$ are: 95 G for L = H_2O,[18] 93 G for L = CH_3NO_2,[19] 92 G for L = CH_3CN,[18] 91 G for L = C_5H_5NO,[20] 90 G for L = pentamethylene tetrazole.[19]

Evidence about small distortions of the octahedron $M(L)_6^{2+}$ was concluded from the zero-field splittings of the Ni^{II} solvates, that are also given in Table III. The observed D values are rather small compared with literature values[11,14] and are indicative for a very slight distortion of the octahedron; only in a few cases smaller values of D were observed.[1,21]

Regarding the EPR spectrum of $Cu(NMIz)_4(ClO_4)_2$, the g value is only approximate, because of the asymmetric resonance line. Further measurements of Cu^{II} in NMIz environment, especially at low temperatures and diluted in diamagnetic lattices are in progress.

No EPR spectra of the Fe^{II} and Co^{II} could be observed in the present circumstances. Presumably temperatures as low as liquid helium are required observe the spectra of these solvates. In any case the observed values of μ fall in the ususal range of octahedral Co^{II} and Fe^{II}, whereas the temperature dependence of the magnetic moment of $Co(NMIz)_6(ClO_4)_2$ is a further indication for octahedral Co^{II}.[13]

Infrared and raman spectra. The vibrational spectrum of *N*-methyl imidazole has recently been described by Perchard and Novak,[3] and assignments for the observed bands were proposed.

Since it is well known that many ligands show band shifts upon complexation[20,22-24] to several metal ions, it was interesting to see whether or not such shifts occurred in our NMIz solvates, with respect to the free ligand. In Table IV the absorptions for the free ligand (liquid), the frequency shifts in the several metal solvates and the assignments are listed. From this Table it is seen that only a few ligand bands show quite large shifts upon complexation. Some of these bands appeared to be dependent upon the metal ion to which NMIz was coordinated. These absorptions are separatedly listed in Table V with increasing shifts for the several solvates, together with the far-infrared and raman vibrations of those solvates, including metal-nitrogen vibrations.

As is easily seen from Table V, the sequence of metal ions corresponds very well with previous ones, found for other ligands,[20,23,24] and also with the well-known Irving-Williams stability series;[25] these sequence is caused by differences in bonding properties of the several metal ions. The underlined bands in Table V are tentatively assigned to infrared active M–N stretching vibrations. However, because of the fact that also the free ligand has an absorption band in the 200-300 cm^{-1} region, the assignments of the M–L stretches in this region are rather uncertain. Considerably mixing between M–L stretching vibrations and ligand modes will certainly be present, and specially in the case of the cobalt and iron compounds a straightforward assignment is not possible.

To see if our infrared active M–N stretches agreed with literature values, Table VI has been set up. In this Table M–N stretches in solvates of formula $M(L)_m^{2+}$ have been gathered for a number of nitrogen donor ligands. Inspection of this Table shows that the sequence of metal ions is nearly the same for all ligands with increasing M–N stretch, which again supports evidence for the proposed structure of our NMIz solvates, and also confirms the tentative assignments of their spectra.

From Table IV it is further observed that infrared active vibrations due to ClO_4^- and BF_4^- occur at 1090 and 620, and at 1050 and 520 cm^{-1} respectively. From the fact that the infrared forbidden transitions at about 930 and 455 cm^{-1} (for ClO_4^-), and at about 750 and 350 cm^{-1} (for BF_4^-) are observed only in the raman spectra, it may be concluded that these anions are not bonded to the metal ions,[1,22] so it is justified to speak of true solvates, in which only ligands NMIz and no anions are coordinated to the metal ions.

Conclusions

Regarding the results given above, the following conclusions can be drawn:

1. *N*-methyl imidazole appears to be a strongly coordinating ligand towards several divalent metal ions and Ag^I. Solvates containing six (or in a few cases four or two) NMIz ligands per metal ion can be prepared with anions like ClO_4^- and BF_4^-.

2. The molecule NMIz appears to be coordinated to metal ions *via* the lone pair orbital of the « pyri-

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Table IV. Vibrational spectra of NMIz and its metal solvates (cm^{-1})

Liquid ligand[3]			Metal solvates of NMIz	
Raman	Infrared	Assignments[3]	Raman	Infrared
3128	3131 w	C—H stretching	n	3135-3150 sh
3103	3105 m	C—H stretching	n	3120-3135 s
3000	3009 sh			
	2986 sh	CH_3-stretchings	n	a
2951	2952 m			
	1675 w	combination bands	n	1675-1695 w
	1589 w			1615-1620 w
1510	1518 s	ring stretching (R_1)	n	1518-1536 s
1500	1506 sh	ring stretching (R_2)	n	1505-1522 s
1472	1463 w	CH_3 bending	n	1470 sh a
1420	1421 m	CH_3 bending	n	1408-1418 m
1353	1361 w	ring stretching (R_3)	n	1365-1370 m
1328	1328 w	ring stretching (R_4)	n	1330-1340 w
1288	1286 s	In plane C—H bending	n	1290-1296 s
1230	1232 vs	ring stretching (R_5)+CN stretch	n	1234-1250 s
1105	1109 s	In plane C—H bending	1105-1115 sh	1105-1115 sh
—	—	ν_3 of the ClO_4^- anion	1080-1090 m, b	1085-1090 vs
—	—	ν_3 of the BF_4^- anion	1040-1070 m, b	1050-1065 vs, b
1075	1078 vs	In plane C—H bending	c	c
1025	1029 m	CH_3 deformation	1027-1029 m	1027-1030 m
904	909 s	ring stretching (R_6)	930- 950 w	930- 960 s
—	—	ν_1 of ClO_4^- anion	929- 931 vs	—
847	860 sh	Out of plane C—H bending	858- 864 w	860- 880 vw
818	821 s	Out of plane C—H bending	830- 840 w	774- 776 sh
				766- 768 vs
740	744 s	Out of plane C—H bending	768- 775 w	—
—	—	ν_1 of BF_4^- anion	742- 750 w	672- 678 m
665	665 vs	ring stretching and CN str.	670- 672 s	655- 660 s
616	618 s	ring deformation	620-623 m	619- 621 m
—	—	ν_4 of ClO_4^- anion		619- 622 vs
—	—	ν_4 of BF_4^- anion	510- 515 vw	515- 520 m
—	—	ν_2 of ClO_4^- anion	450- 460 m, b	—
353	355 w	C—N deformation	365- 385 m	360- 390 m
—	—	ν_2 of BF_4^- anion	345- 355 vw	—
220	224 w	C—N deformation	230- 250 w	220- 240 m
—	—	M—N vibrations	below 325 w s	below 325 w-s

n = not investigated in this region; c = obscured by anion absorptions; a = obscured by nujol absorptions; w = weak; m = medium; s = strong; v = very; b = broad; sh = shoulder.

Table V. Metal-ion dependence of NMIz and metal-nitrogen vibrations in solvates $M(NMIz)_m(anion)_n$, (cm^{-1})

Metal ion	Number of ligands	R_6 (IR) vibr.	C—N deformation		Bands* below 350 cm^{-1}	
			IR	Raman	IR	Raman
Ca	6	930	360	365	$\underline{253}$ vs, 225 sh	240 vw
Cd	6	932	362	366	237 w, $\underline{160}$ s, 145 sh	230 m, 190 w
Mn	6	934	366	368	234 sh, $\underline{211}$ vs	234 w, 190 m, b
Zn	6	935	368	370	237 w, $\underline{186}$ s	245 w, 190 w, 133 m
Fe	6	936	368	370	$\underline{240}$ sh, $\underline{230}$ sh, $\underline{223}$ s	180 w
Co	6	937	372	372	$\underline{245}$ sh, $\underline{226}$ s	240 w, 188 w, 140 w, 102 w
Ni	6	939	377	374	$\underline{262}$ s, 234 m, 184 w	190 m, b
Cu	4	952 sh 956	372 388	—	$\underline{303}$ s, 260 s, 216 s	—
Zn	4	960	369	371	$\underline{274}$ s, 255, 235 sh	246 w, 198 w, 170 sh, 157 m
Mg	6	938	374	371	$\underline{321}$ vs, 238 w, 172 w	246 w, 167 w, 137 m
Ag	2	930 sh 948	362	366	238 w	200 vw, b

* For the meaning of w, m etc. see Table IV; raman spectra of the Cu solvates could not be obtained, since the laser beam destroyed the deep purple compounds; generally the position of the raman bands below 200 cm^{-1} is rather uncertain because the bands were observed as shoulders on the exciting band.

dine nitrogen », rather than *via* that of the « pyrrole nitrogen ».

3. Infrared spectra, magnetic measurements and ligand-field spectra indicate the presence of rather regular octahedrons $M(N)_6^{2+}$ in most of the solvates.

4. NMIz occurs rather high (large value of Dq) in the spectrochemical series and rather low (small value of B) in the nephelauxetic series, which agrees with a rather strong metal-ligand bond.

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Table VI. Comparison of metal-nitrogen stretches for solvates of formula M(ligand)$_n$(anion)$_2$; bands in cm^{-1}

Metal ion M^{2+}(L)$_n$	Number of ligands	Ligand[a]				
		NH$_3$[26,27]	CH$_3$CN[28]	Pyrazole[1]	Imidazole[1]	NMIz[b]
Cd	6	277	204	170	165	160
Zn	6	282	214	202	200	186
Mn	6	295	237	221	214	211
Fe	6	306	246	235	232	228
Co	6	312	252	241	238	232
Ni	6	322	269	264	262	262
Mg	6	—	330	330	322	321
Cu	4	430	325	287	295	282
Zn	4	410	—	—	272	265

[a] In most cases the anions are ClO$_4^-$, except for NH$_3$ where the iodide anion was chosen; [b] Present investigation; in the case of split bands, the averaged value has been taken.

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