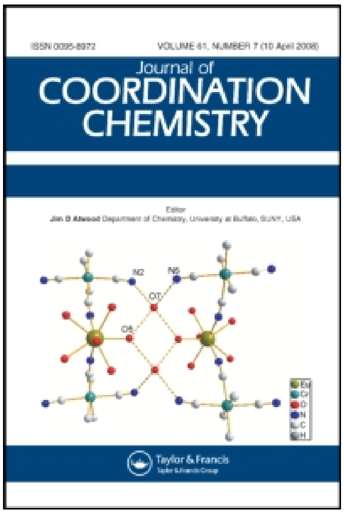

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REACTIVITY OF NITROSODICYANOMETHANIDE TOWARDS Ni(II)

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REACTIVITY OF NITROSODICYANOMETHANIDE TOWARDS Ni(II)

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From the system Ni(II)-$ONC(CN)_2^-$-L, where L = pyrazole (pz), 3(5)-methylpyrazole, 3,5-dimethylpyrazole, 3,4,5-trimethylpyrazole (tmpz) and indazole in aqueous and aqueous-methanolic media, compounds of two types were isolated. Nitrosodicyanomethanide compounds of the type $[Ni\{ONC(CN)_2\}_2L_4]$, according to spectroscopic results, have octahedral structures with nitroso nitrogen bonded $ONC(CN)_2^-$ anions. Compounds of the second type, $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2L_2]$, where L = pz, H_2O, tmpz, contain anionic chelate ligands $NO(CN)CC(OCH_3)NH^-$ which arise by nucleophilic addition of methanol oxygen to the cyano carbon of $ONC(CN)_2^-$ in the Ni(II) coordination sphere. This was established by X-ray crystallography of compounds with L = pz and H_2O. The compound $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$ is triclinic, space group $P\bar{1}$, with a = 5.007(1), b = 6.576(3) and c = 10.721(3) Å, α = 75.63(3), β = 86.79(2) and γ = 78.65(2)°, and Z = 1. Full-matrix least-squares refinement gave R = 0.0372 and Rw = 0.0973 for 1304 reflections. The Ni(II) environment is a slightly elongated rhombic bipyramid, the anionic ligands forming five-membered rings with water molecules in axial positions. The compounds with L = pz or tmpz (as hemihydrates) show the same anionic ligands, but pz or tmpz molecules are located in *cis*-position.

KEYWORDS: nitrosodicyanomethanide, nucleophilic addition, anionic chelate ligand, five-membered metallocycle, X-ray structure

INTRODUCTION

Recently we ascertained[1] that reaction of dicyanamide group with methanol in the Cu(II) coordination sphere leads to formation of an anionic chelate ligand. By this fact we were stimulated to investigate many systems involving transition metals M(II) (M = Cu, Ni, Co, Pd, Pt) with non-linear pseudohalide anions (dicyanamide, tricyanomethanide and nitrosodicyanomethanide) and heterocyclic nitrogen ligands. In the course of this reseaerch we isolated, besides pseudohalide complexes, compounds in which a significant reorganization of the electronic system in the anionic ligands occurred. We found that the greatest disposition towards reaction

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with nucleophilic reagents was exhibited by nitrosodicyanomethanide, as opposed to dicyanamide, whose reaction with methanol is specific[1].

In this paper we present the results obtained in a study of the systems Ni(II)-$ONC(CN)_2^-$-L, where L = pyrazole (pz), 3(5)-methylpyrazole (mpz), 3,5-dimethylpyrazole (dmpz), 3,4,5-trimethylpyrazole (tmpz) and indazole, *i.e.*, benzopyrazole (inz) in aqueous and aqueous-methanolic media. A note concerning the compound isolated from the system with L = pz has already appeared[2].

EXPERIMENTAL

Preparation Procedures

Nitrosodicyanomethanide compounds

A solution of 5.0 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 8 cm^3 of water and a solution of 11 mmol of pyrazole base in 4 cm^3 of water were poured into a solution of 1.0 mmol of $KONC(CN)_2$ in 5 cm^3 of water. On continuous stirring the compound precipitated in the form of a microcrystalline powder. In the cases of $[Ni\{ONC(CN)_2\}_2(mpz)_4]$ and $[Ni\{ONC(CN)_2\}_2(tmpz)_4]$, oily substances were formed, which, after a short time with stirring, changed into microcrystalline precipitates.

Compounds formed by nucleophilic addition

A solution of 5.0 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 25 cm^3 of water and a solution of 10.0 mmol of $NaONC(CN)_2$ in 25 cm^3 of water were poured into a solution of 10.0 mmol of pyrazole base in 50 cm^3 of methanol (in the case of dmpz, 5 cm^3 of water was added at the beginning). Yellow green solutions initially formed changed colour to red brown. From these mixtures crystals separated.

Analyses

Metals were determined chelatometrically after decomposition of the compounds by H_2SO_4 and oxidation of the organic component by $K_2S_2O_8$. Elemental analyses were carried out using a Carlo-Erba analyser. Analytical results and other characteristic data are listed in Table 1.

X-Ray Data Collection and Solution of the Structure of $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$

A single crystal (0.3 x 0.1 x 0.03 mm) was selected for the crystallographic study. Accurate cell parameters were obtained by least-squares refinement of the setting angles of 25 reflections at medium ϑ ($10° \leq 2\vartheta \leq 30°$), using filtered MoKα radiation and an Enraf-Nonius CAD4 diffractometer. Some 2408 independent reflections ($\vartheta_{max} = 26°$) were collected at room temperature, using the ω-2ϑ scan mode. The intensities of three standard reflections were monitored every 3 h; no significant systematic fluctuation was found. The program DIFABS[3] ($\mu = 1.49\ mm^{-1}$) for absorption correction was used; 1304 reflections with $F_o > 4\sigma(F_o)$ were considered observed; $R_{int} = 0.024$ and $R(\sigma) = 0.030$. The structure was solved by Pattersons methods using

Table 1 Analytical data and other properties of the complexes.

Compound	Colour	Dec. T. (°C)[a]	% C		% H		% N		% Ni	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[Ni\{ONC(CN)_2\}_2(pz)_4]$	light brown	160	41.65	40.92	3.11	3.02	37.78	37.32	11.31	11.10
$[Ni\{ONC(CN)_2\}_2(mpz)_4]$	cinnamon brown	138	45.94	45.32	4.21	4.32	34.09	33.45	10.21	10.16
$[Ni\{ONC(CN)_2\}_2(tmpz)_4]$	beige	158	52.42	51.95	5.87	5.73	28.53	28.37	8.54	8.58
$[Ni\{ONC(CN)_2\}_2(inz)_4]$	green-yellow	140	56.77	56.12	3.36	3.29	27.26	26.70	8.16	8.16
$[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(pz)_2] \cdot 1/2H_2O^2$	red-violet	50	36.85	37.04	3.75	3.68	30.71	30.70	12.86	12.97
$[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$	rose-violet	100	27.70	28.00	3.48	3.54	24.22	24.22	16.92	16.85
$[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(tmpz)_2] \cdot 1/2H_2O$	rose-violet	75	44.44	44.13	5.41	5.36	25.91	26.07	10.86	10.94

[a]Determined with 100 mg of samples using a heating rate of 6°C/min.

Table 2 Crystal and refinement data.

Formula	$[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$
M_r	346.95
crystallographic system	triclinic
space group	$P\bar{1}$
a(Å)	5.007(1)
b(Å)	6.576(3)
c(Å)	10.721(3)
α(°)	75.63(3),
β(°)	86.79(2),
γ(°)	78.65(2)
V(Å^3)	335.3(2)
Z	1
D_x (g cm^{-3})	1.718
λ MoKα (Å)	0.71069
$\mu(MoK_\alpha)(mm^{-1})$	1.486
No. of indep. refl.	2408
No. of indep. refl. above $4\sigma(F_o)$	1304
R	0.0372
R_w^{a}	0.0973
$\Delta\rho_{min}$(e Å^{-3})	-0.58
$\Delta\rho_{max}$(e Å^{-3})	+0.91

$^a w = 1/[s^2(F_o^2) + (0.0390P)^2 + 0.5844P]$, where $P = (F_o^2 + 2F_c^2)/3$.

SHELXS86[4] and refined on F^2 by SHELXL93.[5] A difference map of the anisotropically refined structure gave the positions of all hydrogen atoms which were constrained: N-H = 0.86 Å; C-H = 0.96 Å with U(H) = 1.2 U_{eq} (C or N). In the final cycle of full-matrix least-squares refinement R = 0.037 and wR_w = 0.097. Table 2 summarizes crystal and structure refinement data; final atomic parameters are given in Table 3.

Physical Measurements

I.r. spectra (4000–200 cm^{-1}) were recorded using a Philips Analytical PU9800 FTIR spectrometer in KBr pellets and Nujol mulls. Electronic spectra were obtained as described previously[6].

Table 3 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (A^2×10^3) for $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$.

Atom	x/a	y/b	z/c	U_{eq}^{a}
Ni	0	0	0	22(1)
C(1)	2137(6)	-2374(5)	2405(3)	27(1)
C(2)	376(7)	-3723(5)	2093(3)	28(1)
C(3)	4909(8)	-1970(7)	4015(4)	43(1)
C(4)	106(7)	-5741(6)	2913(3)	35(1)
N(1)	2268(5)	-615(4)	1611(3)	29(1)
N(2)	-1026(5)	-2893(4)	1032(3)	27(1)
N(3)	-140(9)	-7353(6)	3537(4)	58(1)
O(1)	3371(6)	-3241(4)	3526(2)	41(1)
O(2)	-2673(5)	-3961(4)	716(2)	34(1)
O(3)	-3216(5)	1811(4)	879(2)	31(1)

$^a U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

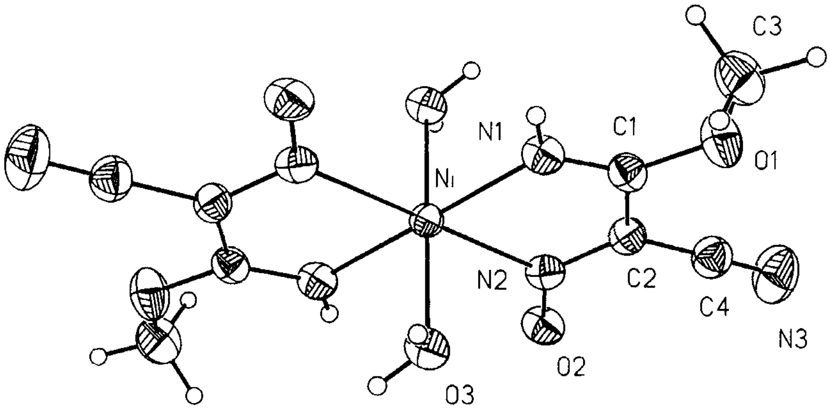


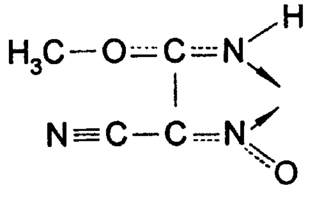
Figure 1 ORTEP drawing[7] of $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$ probability thermal elipsoids drawn at 50%.

RESULTS AND DISCUSSION

Description of the Structure of $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$

The crystal structure of $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$ consists of discrete molecules (Fig. 1), in which the central Ni(II) atom is coordinated by four nitrogen atoms from two bidentate anionic chelate ligands and by two oxygen atoms from water molecules (for important bond lengths and angles see Table 4). The central Ni(II) atom occurs in a special crystallographic position and forms by bonding with the N1 and N2 atoms (the bond lengths Ni-N1 and Ni-N2 are 2.032(3) and 2.093(3) Å, respectively) five-membered, planar rings. The present chelate ligands are in substance the same as those ascertained by X-ray crystallography in $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(pz)_2]$.[2] The bonding situation in these ligands according to the respective bond lengths is approximately such as shown in (*1*). From the Ni-O3 distance, 2.129(2) Å, it follows that the coordination polyhedron is a slightly elongated rhombic bipyramid (point group of the NiN_4O_2 chromophore is D_{2h}).

There is a strong hydrogen bonding between the H32 of water and O2 from an adjacent molecule (see Table 4). A weaker hydrogen bond is formed by H31 and O2 from another molecule. Further hydrogen bonding occurs between H1 of the chelate ligand and O3 of an adjacent water molecule.



(*1*)

Table 5 Important vibrational frequencies for the nitrosodicyanomethanide complexes.

Compound	$\nu(C\equiv N)$	$\nu_{as}(CNO)$		$\nu_s(CNO)$	$\nu(C\text{-}C)$		$\nu(Ni\text{-}N)$			
$[Ni\{ONC(CN)_2\}_2(pz)_4]$	2219vs	1401w[a]	1366s[a]	1350ms	1207ms	1197ms	310m	294ms	263s	253sh
$[Ni\{ONC(CN)_2\}_2(mpz)_4]$	2227vs 2217s	1390vs		1366vs	1207vs	1197sh	308m	249s		
$[Ni\{ONC(CN)_2\}_2(tmpz)_4]$	2218vs	1385s		1366s	1213ms[b]	1207sh[b]	315mw	239ms		
$[Ni\{ONC(CN)_2\}_2(inz)_2]$	2235m 2219vs	1395s		1346s	c	c	287s	261m		

[a] Cannot be distinguished with certainty from the lignd band. [b] One of these absorptions can be due to the ligand vibration.
[c] Not assigned owing to the interference with ligand bands.

Table 4 Selected interatomic distances (Å), angles (°) and hydrogen bonds (Å,°) with e.s.d.'s in parentheses.

Ni-N1	2.032(3)	N1-Ni-N2	79.1(1)
Ni-N2	2.093(3)	N1-Ni-O3	89.6(1)
Ni-O3	2.129(2)	N2-Ni-O3	88.0(1)
N1-C1	1.265(4)	Ni-N1-C1	114.7(2)
C1-C2	1.471(4)	N1-C1-C2	118.2(3)
C2-N2	1.310(4)	C1-C2-N2	115.1(3)
C1-O1	1.325(4)	C2-N2-Ni	112.6(2)
O1-C3	1.443(4)	C1-O1-C3	117.7(3)
C1-C4	1.425(5)	C2-C4-N3	178.2(4)
C4-N3	1.130(5)		
D-H...A	D...A	H...A	D-H...A
O3-H32...O2^{i}	2.65(3)	1.87(4)	174(4)
O3-H31...O2^{ii}	2.809(4)	2.11(5)	149(4)
N1-H1...O3^{iii}	2.979(4)	2.262(4)	141(3)

Symmetry code: (i) $-1-x, -y, -z$; (ii) $x, 1+y, z$; (iii) $1+x, y, z$.

New Ligand Formation in the Coordination Sphere

As in the case of $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(pz)_2]$,[2] the anionic chelate ligand in $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2(H_2O)_2]$ is formed by nucleophilic addition of the methanol oxygen to the cyano carbon of the nitroso nitrogen coordinated[8] $ONC(CN)_2^-$ anion. This carbon possesses some positive charge which activates it for electrophilic function. The methanol proton is transferred to the nitrogen linked with the attached carbon and becomes markedly acid in character.

Intermediate formation of the complex $[Ni\{ONC(CN)_2 \cdot (dmpz)_2]$ in solution is assumed, in which the nucleophilic addition comes about, attended by replacement of the dmpz ligands by water molecules, occupying axial *trans*positions. This makes a difference to the complex isolated from the analogous system with pz,[2] in which the pz ligands remain preserved but arranged in *cis* positions. The presumption of the formation of the Ni(II)-dmpz complex as intermediate is supported by the fact that without the pyrazole base the coordination sphere reaction is not realized.

In a further analogous system with tmpz, according to i.r. spectroscopy (see below), a complex of the same anionic ligand is formed, but still containing in the coordination sphere two tmpz ligands. These are very likely located in *cis* positions, as in the Ni(II)-pz complex.[2]

Infrared Spectra

In the i.r. spectra of the nitrosodicyanomethanide compounds, the bands characteristic of the $ONC(CN)_2$ ligand, and those of the Ni-N stretching vibrations were assigned (Table 5). The $\nu_{as}(NCO)$ and $\nu_s(NCO)$ vibrations are markedly shifted to higher frequencies with respect to those of the free anion[9]. This fact suggests that in the $[Ni\{ONC(CN)_2\}_2L_4]$ complexes the anion is bonded through the nitrogen of the nitroso group.[8,9] Changes of other nitrosodicyanomethanide frequencies are slight.

In the far - i.r. region (to 200 cm^{-1}) two, and in one case four, absorptions are found which can be ascribed to Ni-N stretching at about 305 and 255 cm^{-1}. It can be accepted that the former frequencies belong mainly to Ni-N(nitroso) stretches, while the latter are Ni-N(L) stretches.[10] The latter frequencies are rather variable, this being understandable in view of the varying basicity as well as steric properties of the respective pyrazole ligands.

In the i.r. spectra of the chelate complexes $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2L_2]$ most of the bands belonging to the anionic chelate ligand as well as the bands of the Ni-donor stretches were tentatively assigned (Table 6). The most striking feature of these data is the presence of C≡N and C=N stretching vibration bands at *ca* 2215 and 1645 cm^{-1}, respectively. A further characteristic is the presence of bands between *ca* 3345–3255 cm^{-1}, which can be ascribed to NH stretches in the anionic ligand. Complexes with L = pz and tmpz show still other, much less intense and split NH stretching bands around 3140 cm^{-1}, originating from the pyrazole ligands. On the other hand, we were not able to identify for the diaqua-complex the vibration bands of coordinated water, with the exception of the very weak one at 529 cm^{-1}, corresponding to wagging.[11] In the region between *ca* 600–400 cm^{-1} several medium intensity bands occur (not included in Table 6), which are apparently due to ring deformations of the chelate ligand.

The far -i.r. region contains bands between *ca* 300–260 cm^{-1}, which are assigned to the stretching vibrations of the Ni-N bonds. For complexes with pyrazole ligands, less intense bands at ≈250 cm^{-1} in all likelihood belong to the Ni-N(L) stretches.[12] Finally, in the case of the diaqua complex, the band at 332 cm^{-1}, being absent in the spectra of the preceding compounds, is reasonably ascribed to the $Ni\text{-}OH_2$ stretch.[11]

Solid State Electronic Spectra

Electronic spectroscopic data including ligand field and intraligand absorptions are listed in Table 7. The ligand field spectra of the nitrosodicyanomethanide complexes consist of three spin-allowed absorptions, whose positions are typical for octahedral configurations[13] and they are assigned in order of increasing energy to the $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and $^3T_{2g}(P) \leftarrow {}^3A_{2g}$ transitions. Between the bands of the first two transitions weak absorptions occur which very likely belong to the

Table 6 Important vibrational frequencies (cm^{-1}) for the chelate complexes $[Ni\{ONC(CN)_2 \cdot CH_3OH\}_2L_2]$.

L = pz[a]		L = H_2O		L = tmpz[a]		Assignment
3611 w,b	3509 vw	3548 vw	3514 vw	3625 vw,b	3490 w	ν(OH)
3449 vw	3390 vw					
3319 s	3156 sh	3373 sh	3345 vs	3335 sh	3255 vs	ν(NH)
3135 w	3119 sh			3168 sh	3110 sh	
2220 ms		2215 s		2217 ms		ν(C≡N)
1646 vs		1650 vs		1643 vs		ν(C=N)
1419 s		1429 s	1397 m	1415 s		$\delta(CH_3)$
1303 sh	1296 m	1288 vs		1296 sh[b]	1282 vs	ν(ONC)
1200 s	1168 mw	1220 sh	1205 s	1202 s[b]	1157 m	ν(COC),
1211 s		1157 m	1129 vs	1126 vs		ν(C-C)
767 s		779 vs		779 vs		γ(NH)
		529 vw				$\rho_w(H_2O)$
		332 mw				ν(Ni-O)
291 sh	272 s	301 mw	261 s	297 sh[b]	279 m[b]	ν(Ni-N)
251 w				250 mw[b]		

[a] In form of a hemihydrate. [b] Cannot be distinguished with certainty from the bands of tmpz.

Table 7 Electronic spectroscopic data for the complexes.

Compound	ν_{max} (μm^{-1})			10Dq (μm^{-1})	B (μm^{-1})	β
[Ni{ONC(CN)$_2$}$_2$(pz)$_4$]	1.04	≈1.32sh	≈1.72sh,b 2.09 2.67	1.04	0.0803	0.78
[Ni{ONC(CN)$_2$}$_2$mpz)$_4$]	1.02	≈1.33sh	≈1.67sh,b 1.99b 2.60 ≈2.90sh	1.02	0.0772	0.75
[Ni{ONC(CN)$_2$}$_2$(tmpz)$_4$]	1.03	≈1.31sh	≈1.74sh,b 2.15 ≈2.67sh ≈2.99sh	1.03	0.0817	0.79
[Ni{ONC(CN)$_2$}$_2$(inz)$_4$]	1.04	≈1.32sh	1.77 2.21 2.71	1.04	0.0837	0.81
[Ni{ONC(CN)$_2$·CH$_3$OH}$_2$(pz)$_2$]·1/2H$_2$O	≈1.15sh	1.27	1.86 ≈2.52sh ≈2.84sh	1.27	0.0567	0.55
[Ni{ONC(CN)$_2$·CH$_3$OH}$_2$(H$_2$O)$_2$]	≈1.25sh	1.34	1.96 ≈2.58sh,b	1.34	a	a
[Ni{ONC(CN)$_2$·CH$_3$OH}$_2$(tmpz)$_2$]·1/2H$_2$O	≈1.12sh	1.21	1.85 ≈2.43sh,b ≈2.79sh	1.21	0.0637	0.62

[a] See text.

Figure 1 ORTEP drawing[7] of [Ni{ONC(CN)$_2$·CH$_3$OH}$_2$(H$_2$O)$_2$] probability thermal elipsoids drawn at 50%.

spin-forbidden $^1E_g \leftarrow {}^3A_{2g}$ transition[13]. The 10 *Dq* values fluctuate in a relatively small range of about 1.03 μm^{-1}. The β values, indicating a significant amount of covalency,[14] are also rather close each other.

It can be concluded that the $[Ni\{ONC(CN)_2\}_2L_4]$ complexes have an octahedral nitrogen environment for the central Ni(II) atom, comprising the tertiary nitrogens of four pyrazole ligands and the nitroso nitrogens of two nitrosodicyanoamides, located very likely in *trans* positions. Similar structures were ascribed on the basis of the spectroscopic results to $[M^{II}\{ONC(CN)_2\}_2L_4]$ complexes with M = Cu, Co, L = pz and M = Co, L = mpz, inz.[15]

In the high energy region (above ≈2.0 μm^{-1}) some absorptions correspond to transitions in the coordinated nitrosodicyanomethanide,[16] but they are clearly distinguishable from the *d-d* absorptions. The chelated Ni(II) complexes have also three octahedral ligand field absorptions,[13] but in comparison with the preceding group of complexes these are shifted to higher energies, in particular those of the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition (by *ca* 0.25 μm^{-1}). On the bands corresponding to the latter transition, low energy shoulders are observed and which can be attributed to the $^1E_g \leftarrow {}^3A_{2g}$ transition,[13] shifted with respect to the nitrosodicyanomethanide complexes to lower energies. The highest energy *d-d* transitions, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, appear as shoulders at *ca* 2.8 μm^{-1}; however, in the case of the diaqua complex the shoulder is not resolved. Further shoulders, occurring ca 0.3 μm^{-1} lower, very likely belong to some transition inside the anionic ligand.

The $^3T_{2g} \leftarrow {}^3A_{2g}$ transition energies indicate strong ligand fields with 10 *Dq* values about 1.27 μm^{-1}. These fields are produced mainly by the anionic chelate ligand, although the variability of the 10 *Dq* values reveals that other factors exert influence, especially the two neutral ligands. Apparently, two aqua ligands in *trans* positions have a stronger perturbation effect on the ligand field splitting than the *cis* pz and tmpz ligands (with considerable steric bulk).

The β values, calculated for the complexes with pyrazole ligands (where the third transition is resolved), are extremely low. This fact suggests a high degree of covalency, which is to be expected in the respective chelate systems. Nevertheless, no great importance may be ascribed to the obtained values, mainly because of the inaccurate determination of the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition energy as well as theoretical simplifications.[14]

SUPPLEMENTARY MATERIAL

Tables of thermal parameters, H atom positions and observed and calculated structure factor amplitudes are available from the authors upon request.

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