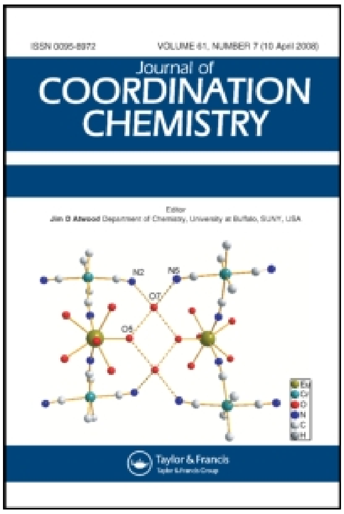

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COMPLEXES ISOLATED FROM SYSTEMS OF Ni(II) OR Co(II) WITH NCO⁻ AND PYRAZOLE TYPE LIGANDS. NOVEL EXAMPLES OF NUCLEOPHILIC ADDITION IN THE METAL COORDINATION SPHERE AND OF COLIGAND ISOMERISM

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COMPLEXES ISOLATED FROM SYSTEMS OF Ni(II) OR Co(II) WITH NCO^- AND PYRAZOLE TYPE LIGANDS. NOVEL EXAMPLES OF NUCLEOPHILIC ADDITION IN THE METAL COORDINATION SPHERE AND OF COLIGAND ISOMERISM

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From M(II) - NCO^- - L systems [M(II) = Ni(II), Co(II); L = pyrazole (pz), 3,5-dimethylpyrazole (dmpz), 3,4,5-trimethylpyrazole (tmpz)] the following new solid compounds were prepared: $Ni(NCO)_2L_4$, $Ni(NCO)_2(tmpz)_2$, $Ni(tmpz.NCO)_2$, $Co(NCO)_2(pz)_4$, and $Co(NCO)_2L_2$, where L = dmpz, tmpz. Spectroscopic and magnetic data were used for the purpose of assigning probable structures to the compounds. For $Ni(NCO)_2L_4$, where L = dmpz, tmpz, and $Ni(NCO)_2(tmpz)_2$ polymeric structures with N-bridging NCO groups are accepted, in the case of the 1:4 compounds with two L molecules out of the coordination sphere. Planar $Ni(tmpz.NCO)_2$ contains 3,4,5-trimethyl-1-carbamoylpyrazolate anions as chelate ligands, formed by C(NCO) - N(*imine) nucleophilic addition in the* Ni(II) coordination sphere; this compound is a coligand isomer of $Ni(NCO)_2(tmpz)_2$. Also, the compound $Co(NCO)_2(pz)_3$ was isolated, in which equilibria between the Co(II) - pz.NCO and Co(II) - NCO species were ascertained.

Keywords; nickel, cobalt, pyrazole, complexes, cyanate, nucleophilic addition

INTRODUCTION

A topical aspect of cyanate coordination chemistry is the possibility of nucleophilic addition of the cyanate carbon at the imine nitrogen of the pyrazole type ligand in the metal coordination sphere. This reaction leading to the formation of new anionic chelate ligands was thoroughly investigated for Cu(II) using pyrazole and its various derivatives, especially 3,5-di- and 3,4,5-trimethylpyrazole.[1] In order to ascertain what influence is exerted by the central atom on the ucleophilic addition we set out to study analogous systems with Ni(II) or Co(II) central atoms. In this contribution we report the results obtained from systems of Ni(II) or Co(II) with NCO^- and pyrazole type bases (L).[2]

EXPERIMENTAL

Materials

3,5-Dimethylpyrazole was prepared by reaction of 2,4-pentanedione (acetylacetone) with hydrazine sulfate in alkaline solution. 3,4,5-Trimethylpyrazole was synthetized by condensation of 3-methyl-2,4-pentanedione (β-methylacetylacetone) with hydrazine

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sulfate in alkaline medium. 3-Methyl-2,4-pentanedione was prepared by methylation of 2,4-pentanedione with the aid of methyl iodide as the alkylation agent.

Other chemicals used were commercial preparations (Lachema or Fluka).

Preparation of the Complexes

$Ni(NCO)_2L_4$.

An aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ together with an aqueous solution of KOCN was poured into a methanolic solution of L ligand. During continuous stirring the solid product was precipitated, and was filtered off, washed with methanol and dried over KOH in a desiccator.

The preparation of $Ni(NCO)_2(pz)_4$ was made at room temperature and at 50°; the results were the same in both cases.

$Ni(NCO)_2(tmpz)_2$.

When aqueous solutions of $Ni(NO_3)_2$ and KOCN were added to a warm solution of tmpz in acetone, a precipitate separated upon mixing. It was filtered off, washed with acetone, and dried in a desiccator.

$Ni(tmpz \cdot NCO)_2$.

This compound was formed from the filtrate after separating $Ni(NCO)_2(tmpz)_4$ as a pink voluminous precipitate. It was filtered off and dried over KOH in a desiccator.

Poddar and Roy Chowdhury[3] also prepared $Ni(tmpz \cdot NCO)_2$, but by a different synthesis using 3,4,5-trimethyl-1-carbamoylpyrazole directly.

Solutions used were 1.:4 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 10 cm^3 of water, 10 mmol of KOCN in 10 cm^3 of water, and 13 mmol of pz in 10 cm^3 of methanol; 2.:10 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 30 cm^3 of water, 20 mmol of KOCN in 30 cm^3 of water, and 40 mmol of dmpz in 30 cm^3 of methanol; 3.:3.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 10 cm^3 of water, 6.8 mmol of KOCN in 10 cm^3 of water, and 6.9 mmol of tmpz in 10 cm^3 of methanol; 4.:3.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 4 cm^3 of water, 6.8 mmol of KOCN in 7 cm^3 of water, and 9.1 mmol of tmpz in 20 cm^3 of acetone.

$Co(NCO)_2L_n$ (n = 2 or 4).

Aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and KOCN were poured together into a methanolic solution of L ligand. During continuous stirring a precipitate was formed; after filtering off and washing with methanol it was dried over KOH in a desiccator.

Solutions used were 1.:10 mmol of $Co(NO_3)_2 \cdot 6H_2O$ in 10 cm^3 of water, 20 mmol of KOCN in 10 cm^3 of water, and 40 mmol of pz and dmpz in 20 and 10 cm^3 of methanol, respectively; 2.:35 mmol of $Co(NO_3)_2 \cdot 6H_2O$ in 10 cm^3 of water, 69 mmol of KOCN in 10 cm^3 of water, and 68 mmol of tmpz in 10 cm^3 of methanol.

After separating the rose-red crystals of $Co(NCO)_2(pz)_4$from the filtrate, a brown product was also isolated, with an approximate composition $Co(NCO)_2(pz)_3$. This was filtered off, washed with a methanol-water mixture (1:1) and dried over KOH in a desiccator. The same substance was also prepared by recrystallization of $Co(NCO_2)(pz)_4$ from hot methanol.

Analyses

Elemental analyses were carried out on a CHN-analyzer (Carlo Erba). Nickel and cobalt were determined chelatometrically after destruction of the complexes by the aid of H_2SO_4 and $K_2S_2O_8$. The analytical data together with some other fundamental characteristics of the complexes are presented in Table I.

Physical Measurements

The infrared spectra (4000–400 cm^{-1}) were recorded on an IR-75 (Zeiss, Jena) spectrophotometer using Nujol suspensions. The far infrared (400–50 cm^{-1})[4] and electronic (40000–5000 cm^{-1})[5] spectra, magnetic susceptibilities,[6] thermal decompositions,[7] as well as X-ray diffraction patterns[8] were measured as described in the cited papers.

RESULTS AND DISCUSSION

The reactions between Ni(II) or Co(II), NCO^- and a pyrazole type base yielded a series of complexes with the metal-base ratio of 1:4 or 1:2. These complexes were crystalline powders which analysed well, had reproducible X-ray powder diffraction patterns and were stable on air.

The powder X-ray diffractions showed that the $M(NCO)_2(pz)_4$ complexes are isostructural. The i.r. spectra, being virtually identical, confirm this finding. The differences in the i.r. spectra of both 1:2 Ni(II) derivatives of tmpz enable us to conclude that they are coligand isomers.[1c,d]

According to its i.r. spectral data, $Co(NCO)_2(pz)_3$ contains 1-carbamoylpyrazolate anions as chelate ligands, forming the species $Co(pz\cdot NCO)_2$. However, a certain amount of Co(II) cyanate species with pyrazole is also present in this compound, accounting for its composition and also for some fluctuation in the composition of various samples. Therefore, we made no physical measurements with this compound other than recording the i.r. spectra.

Thermal Decompositions

For all complexes studied TG, DTG, and DTA curves were recorded; decomposition temperatures are listed in Table I. It was ascertained that during decomposition both pz complexes and $Ni(NCO)_2(dmpz)_4$ lost two neutral ligand molecules and only then a complete decomposition came about. The compound $Co(NCO)_2(dmpz)_2$ *totally* decomposed at the decomposition temperature. It is interesting that the decomposition course of $Ni(NCO)_2(tmpz)_2$ and that of its coligand isomer are practically the same. During its decomposition, $Ni(NCO)_2(tmpz)_2$ probably transforms into $Ni(tmpz\cdot NCO)_2$, the latter appearing to be more stable. However, the DTA curve does not show any exothermic effect corresponding to this isomerization, as was observed in analogous Cu(II) complexes.[7] The decomposition course of the remaining complexes is continual, so that little can be said about order and state of the ligands being split off.

Infrared Spectra

The imine and cyanate or carbamoyl vibrational frequencies were determined by

TABLE I
Analytical and other data for the complexes.

Compound	Colour	Dec.T. (°)	% C		% H		% N		% Ni or Co		μ_{eff}[a]
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	(B.M.)
$Ni(NCO)_2(pz)_4$	pale blue	170	40.51	40.19	3.88	3.79	33.75	33.48	14.14	14.23	3.24
$Ni(NCO)_2(dmpz)_4$	pale green	138	50.11	49.99	6.17	6.17	26.57	26.51	11.13	11.43	3.24
$Ni(NCO)_2(tmpz)_4$	green-blue	85	53.53	52.94	6.91	6.91	24.01	23.79	10.06	10.23	3.27
$Ni(NCO)_2(tmpz)_2$	pale green	98	46.31	45.98	5.55	5.57	23.15	22.87	16.17	15.89	3.12
$Ni(NCO \cdot tmpz)_2$	pink	98	46.31	46.02	5.55	5.27	23.15	22.96	16.17	15.94	0.56
$Co(NCO)_2(pz)_4$	rose-red	137	40.49	39.84	3.88	3.83	33.73	33.49	14.19	14.37	5.08
$Co(NCO)_2(dmpz)_2$	blue	237	42.99	41.90	4.81	4.76	25.07	24.92	17.58	17.46	4.62
$Co(NCO)_2(tmpz)_2$	blue	170	46.28	46.48	5.55	5.57	23.13	23.03	16.22	15.99	4.63

[a] Calculated by the relation $\mu_{Eff} = 2.83(\chi_M^{corr} T)^{1/2}$, where χ_M^{corr} is the molar susceptibility in units of $cm^3\ mol^{-1}$, corrected for diamagnetism using Pascal constants.

TABLE II
Important vibrational frequencies in the 4000–400 cm^{-1} region.

Compound	$\nu(NH)$	$\nu_{as}(NCO)$	$\nu(CO)$	$\nu_s(NCO)$	$\nu(CN)$	$\nu(CN_{ring})$	$\delta(NCO)$	$\gamma(NCO)$
$Ni(NCO)_2(pz)_4$	3370s, 3318s	2205sh, 2193vs		1317m			638ms, 613ms	
$Ni(NCO)_2(dmpz)_4$	3374vs, 3350vs	2223vs		1307ms[a]			675mw[a], 664m, 655m, 618s, 611s	
$Ni(NCO)_2(tmpz)_4$	3321sh, 3297s	2218vs, 2199vs		1313m			683w[b], 670w[b], 655vw, 630m, 612m	
$Ni(NCO)_2(tmpz)_2$	3309vs, 3265sh	2207vs		1311sh			681m[b], 668m[b], 640m, 614ms, 593ms	
$Ni(tmpz \cdot NCO)_2$	3417m, 3381ms		1691vs		1325m[a]	1250m		527m
$Co(NCO)_2(pz)_4$	3368s, 3317s	2203vs, 2192vs		1316m			629ms, 613ms	
$Co(NCO)_2(dmpz)_2$	3503mw	2193vs		1331ms, 1326ms[a]			622s, 615s	
$Co(NCO)_2(tmpz)_2$	3517s, 3491s	2245vs, 2215vs		1351m, 1343m			611s	
$Co(NCO)_2(pz)_3$[c]	3472sh,br, 3340s		1665vs		1331m	1209m		527m

[a] Cannot be distinguished from the other ligand vibrations. [b] One of these bands may belong to the pyrazole ligand vibration. [c] Data for the complex containing mostly 1-carbamoylpyrazolate anions only (see text).

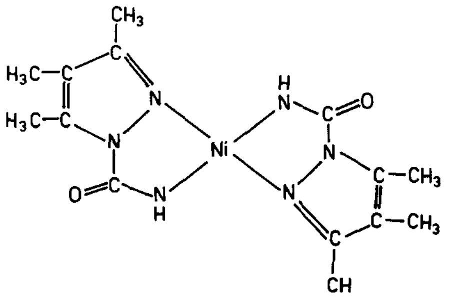

FIGURE 1 Proposed structure of Ni(tmpz· NCO)$_2$.

comparison of the recorded spectra with those of free pyrazole and its derivatives,[9] as well as of other complexes containing pyrazoles as ligands;[1c,9b,10] they are listed in Table II.

The most important fact following from the i.r. spectra is the presence of anionic chelate ligands of the 1-carbamoylpyrazolate type in Ni(tmpz· NCO)$_2$, which is incontestably revealed by the C = O and C–N (ring) stretching, as well as by the NCO out-of-plane bending frequencies.[1] These ligands have been formed, similarly as in the case of the analogous Cu(II) complexes, by the nucleophilic C(NCO)–N(imine) addition in the Ni(II) coordination sphere[1] and gave with this central atom a four-N-coordinate complex (Fig. 1). Driessen *et al.*,[11] studied two closely related compounds, Ni(pz· NCO)$_2$ and Ni(dmpz· NCO)$_2$, prepared by direct synthesis, and attributed to them, on the basis of i.r. evidence, analogous structures. Since cyanate vibrational bands are completely absent in the spectrum, the nucleophilic addition in the Ni(II) - NCO$^-$ - tmpz system is practically complete.

A more complicated situation, however, exists for Co(NCO)$_2$(pz)$_3$. Although its i.r. spectrum contains bands characteristic of the carbamoyl group, other bands also occur, which must be due to the cyanate group vibration.[12] The relative intensities of the ν_{as}(NCO) and ν(CO) bands for various products formed in the Co(II) - NCO$^-$ - pz system indicate that the nucleophilic addition does not go to completion, but probably equilibria are established between Co(II) carbamoylpyrazolate and cyanate species, with a dependence on the preparation conditions used (temperature, solvent *etc.*).

The i.r. spectra of the cyanato complexes studied exhibit the usual bands for nitrogen coordinated NCO groups.[12] In Ni(NCO)$_2$(dmpz)$_4$ and Ni(NCO)$_2$(tmpz)$_4$ the extent of the NCO deformation mode splitting suggests that these groups act as one-end N-bridging ligands.[12] With respect to the stoichiometry and six-coordination of the compounds, in such a bridging case two dmpz and tmpz ligands per Ni(II) atom would be located outside the coordination spheres of the complexes. The steric hindrance of the bulky dmpz or tmpz ligands and also their high basicity would be responsible for this phenomenon, but only X-ray crystallographic studies could provide a conclusive answer.

Except for Co(NCO)$_2$(dmpz)$_2$ and Co(NCO)$_2$(tmpz)$_2$, the N–H stretching frequencies of the pyrazole ligands are significantly lower than those in the corresponding free ligands.[9] Since the coordination site of these ligands is surely the pyridine nitrogen,[10] these shifts may be attributed to hydrogen bond formation with the NCO groups. The split N–H stretches indicate that hydrogen bonds of unequal strengths are present;[10] in Ni(NCO)$_2$(dmpz)$_4$ and Ni(NCO)$_2$(tmpz)$_4$ two kinds of dmpz or tmpz molecules could also contribute.

TABLE III
Vibrational frequencies in the 400–50 cm^{-1} region.

Compound	ν(M–N)	Further bands
$Ni(NCO)_2(pz)_4$	295vs, 249vs	208s, 183s, 104m, 69w,br^a
$Ni(NCO)_2(tmpz)_4$	288sh, 276s, 228vs	346w, 296s, 206sh,br, 194m, 173m, 106w,vbr
$Ni(NCO)_2(tmpz)_2$	275sh,br, 244vs, 231sh	350w, 289s, 205sh,br, 169m,br, 118w, br
$Ni(tmpz \cdot NCO)_2$	309w^{a,b}, 271w^b, 231w	385m, 178mv, 156sh,br, 112sh,br
$Co(NCO)_2(pz)_4$	278vs, 229vs	195s, 167ms, 100mw, 79w,br^a
$Co(NCO)_2(tmpz)_2$	377vs, 343vs, 297vs^b, 290vs^b, 244s	205m, 155s, 136m, 93m

[a] A split maximum, the average frequency is given. [b] About assignment see text.

Far-infrared Spectra

In order to obtain some further evidence for the structures of our compounds, far-i.r. spectra for most of them were recorded. By comparison of these spectra with those of complexes containing corresponding ligands[10,1c] and also with the free ligand spectrum,[1c] the M–N stretching vibrations were assigned (Table III).

The spectra of both $M(NCO)_2(pz)_4$ complexes exhibit two M–N stretching bands indicating *trans*-octahedral configurations with effective D_{4h} symmetry. The lower bands have frequencies around the values usually found for Ni, Co–N(aromatic) stretches[13] and accordingly they are mainly due to the M–N(pz) stretches. Thus, the higher frequency bands must correspond to the M–NCO stretches. The low-frequency shift of both M–N stretches when passing from Ni(II) to Co(II) agrees with the position of these atoms in the Irwing-Williams series.[10,14]

In the spectra of $Ni(NCO)_2(tmpz)_4$ and $Ni(NCO)_2(tmpz)_2$ broad complex absorptions appear between 300–200 cm^{-1}. The 290 cm^{-1} components are most likely free tmpz vibrations[1c] and the lower-frequency patterns may be considered as Ni–N stretches. Their complex character confirms the assumption of a polymeric N(NCO)-bridged structure for both compounds; for example, in $Ni(NCO)_2(3\text{-Br-pyridine})_2$ with the same structure, similar features in the far i.r. were observed.[15]

The $Ni(tmpz \cdot NCO)_2$ spectrum shows three relatively weak bands between 310–230 cm^{-1}. One of the two bands in the proximity of 290 cm^{-1} has probably an internal ligand vibrational nature,[1c] so that the two bands may be ascribed to the Ni–N stretches, suggesting a D_{2h} microsymmetry for the planar Ni(II) chelate species.

For $Co(NCO)_2(tmpz)_2$ one of the two 290 cm^{-1} absorptions belongs to free tmpz; as many as four bands are attributable to Co–N stretching vibrations. This number is consistent with a distorted tetrahedral configuration of the CoN_4 skeleton, corresponding to the point group C_{2v}. The relatively large shift to higher vibrational frequencies with respect to the octahedral complex $Co(NCO)_2(pz)_4$ strongly confirms[16] this structural supposition.

Electronic Spectra and Magnetism

Room temperature magnetic moments and electronic spectral data are given in Tables I, IV and V. The ligand field spectra of $Ni(NCO)_2(pz)_4$ and $Co(NCO)_2(pz)_4$ are

TABLE IV
Electronic spectral data and ligand field parameters for the octahedral and tetrahedral complexes.

Compound	$\tilde{\nu}(10^3\ cm^{-1})$[a]	Assignment[b]	Dq(cm^{-1})	B(cm^{-1})	β
$Ni(NCO)_2(pz)_4$	10.4	$^3T_{2g} \leftarrow {}^3A_{2g}$	1040	854	0.83
	(13.5)	$^1E_g \leftarrow {}^3A_{2g}$			
	16.9	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$			
	(22.7)	$^1T_{1g} \leftarrow {}^3A_{2g}$			
	27.3	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$			
$Co(NCO)_2(pz)_4$	9.4	$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	1060	813	0.84
	(19.1)	$^4A_{2g} \leftarrow {}^4T_{1g}(F)$(?)			
	20.4	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$			
$Co(NCO)_2(dmpz)_2$	7.8[c]	$^4T_1(F) \leftarrow {}^4A_2$	454	752	0.78
	17.1[c]	$^4T_1(P) \leftarrow {}^4A_2$			
	21.9	$D \leftarrow Q$			
	(23.45)	$D \leftarrow Q$			
	24.5	$D \leftarrow Q$			
$Co(NCO)_2(tmpz)_2$	7.5[c]	$^4T_1(F) \leftarrow {}^4A_2$	435	763	0.79
	17.0[c]	$^4T_1(P) \leftarrow {}^4A_2$			
	(22.4)	$D \leftarrow Q$			
	23.9	$D \leftarrow Q$			

[a]The values in parentheses are approximate wavenumbers of shoulders. [b]D = doublet, Q = quartet. [c]The band of a multiplet structure; the maximum is taken in the centre of gravity.

TABLE V
Electronic spectral data and ligand field parameters for the tetragonal-octahedral complexes.

Compound	$\tilde{\nu}$ $(10^3\ cm^{-1})$[a]	Assignment[b]	Dq^E (cm^{-1})	Dq^A (cm^{-1})	Dt (cm^{-1})
$Ni(NCO)_2(dmpz)_4{}^{o}$	(8.5)	$^3B_{2g} \leftarrow {}^3B_{1g}$	850	1050	-114
	9.5	$^3E_g \leftarrow {}^3B_{1g}$			
	(13.5)	$S \leftarrow T$			
	15.4	$^3T_{1g}(F) \leftarrow {}^3B_{1g}$			
	26.5	$^3T_{1g}(P) \leftarrow {}^3B_{1g}$			
$Ni(NCO)_2(tmpz)_4$	(8.6)	$^3B_{2g} \leftarrow {}^3B_{1g}$	860	1050	-109
	9.55	$^3E_g \leftarrow {}^3B_{1g}$			
	(13.25)	$S \leftarrow T$			
	(14.7)	c			
	15.95	$^3T_{1g}(F) \leftarrow {}^3B_{1g}$			
	(22.8)	$S \leftarrow T$			
	26.0	$^3T_{1g}(P) \leftarrow {}^3B_{1g}$			
$Ni(NCO)_2(tmpz)_2$	(7.2)	$^3B_{2g} \leftarrow {}^3B_{1g}$	720	1040	-183
	8.8	$^3E_g \leftarrow {}^3B_{1g}$			
	(12.7)	$S \leftarrow T$			
	15.2	$^3T_{1g}(F) \leftarrow {}^3B_{1g}$			
	25.5	$^3T_{1g}(P) \leftarrow {}^3B_{1g}$			

[a]See Table IV. [b]S = singlet, T = triplet. [c]The assignment is not clear.

typical for octahedral ligand arrangements around Ni(II) or Co(II).[17] The values of the Dq parameter correspond with the position of the respective metals in the spectrochemical series of central atoms.[18] The room temperature magnetic moments are quite normal for octahedrally coordinated Ni(II) or Co(II) (in the high spin state).[19]

On the other hand, the ligand field spectra of $Co(NCO)_2(dmpz)_2$ and $Co(NCO)_2(tmpz)_2$ are diagnostic of their tetrahedral configuration.[17a,20] Accordingly, both Dq and β values are considerably lower than in the octahedral case. The adoptation of tetrahedral stereochemistry is apparently favoured by the steric

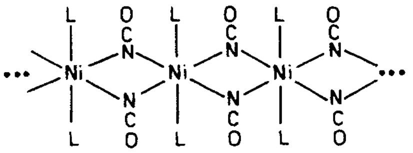

FIGURE 2 Proposed structures of the Ni(NCO)$_2$L$_4$ (L = dmpz, tmpz) and Ni(NCO)$_2$(tmpz)$_2$ complexes.

requirements of the dmpz and tmpz ligands. The decrease of ligand field strength from dmpz to the more basic tmpz is felt to be connected with crystal packing factors due to the additional 3-methyl group. The near-i.r. bands are perceptibly broadened and show a long tail towards lower wavenumbers. This is an evidence for the splitting of the $^4T_1(F)$ state by the lower symmetry (C_{2v}) component of the ligand field,[17a,21] as was already revealed by the Co–N stretching vibrations in Co(NCO)$_2$(tmpz)$_2$ (*vide supra*). The magnetic moments of the latter two complexes are in the range for tetrahedrally coordinated Co(II).[19]

The Ni(II)-dmpz and Ni(II)-tmpz complexes have rather similar d ← d spectra, which are indicative of tetragonal-octahedral coordination geometry.[17a,22] This may be inferred from the broad near-i.r. bands, exhibiting on the low energy side ill resolved shoulders. Thus, the maxima would have to be assigned as transitions to the doubly degenerate ^3E_g state while the shoulders as transitions to the $^3B_{2g}$ state, in D_{4h} symmetry. On the basis of this assignment, the Dq^E and Dq^A parameters (equatorial and axial ligand field strength), as well as the tetragonal parameter, Dt, were calculated. As it can be seen from Table V, the sign of Dt is negative and $Dq^A > Dq^E$. Based on these results and consistent with the i.r. data, we ascribe to all three complexes polymeric chain structures, in which each Ni(II) atom is surrounded by four bridging cyanate nitrogens in the equatorial plane and coordinates two dmpz or tmpz ligands (L) in axial positions (Fig. 2).

According to the Dq^E, Dq^A, and Dt values, in Ni(NCO)$_2$(dmpz)$_4$ and Ni(NCO)$_2$(tmpz)$_4$ the structure-bonding situation is very similar. For Ni(NCO)$_2$(tmpz)$_2$ the $|Dt|$ value is rather higher and the Dq^E value lower than in the previous cases (but the Dq^A value has changed very little). This could mean a weakening of the equatorial bridge > NCO bonds, indicated also by the decrease of the two higher Ni–N stretching frequencies with respect to Ni(NCO)$_2$(tmpz)$_4$. However, in the absence of X-ray crystallographic data we cannot further speculate.

The room temperature μ_{eff} values for Ni(NCO)$_2$(dmpz)$_4$ and Ni(NCO)$_2$(tmpz)$_4$ are very similar and close to the μ_{eff} value of Ni(NCO)$_2$(pz)$_4$. The Ni(NCO)$_2$(tmpz)$_2$ μ_{eff} value is somewhat lower, possibly owing to a stronger tetragonality of the given complex.

The ligand field spectrum of Ni(tmpz·NCO)$_2$ consists of a broad band with the maximum at 20600 cm^{-1} and shoulders at about 17500 and 23000 cm^{-1}; no absorption appears in the near-i.r. region. Such a spectrum suggests a four-coordinate planar configuration of the Ni(II) chelate,[17a] as was proved for α-Cu(dmpz·NCO)$_2$[1a] and assumed for α-Cu(tmpz·NCO)$_2$.[1c] The d ← d band corresponds to the several transitions from the e_g, b_{2g}, a_{1g} orbital set to the antibonding b_{1g} orbital. The shoulders on both the low and high energy sides of this band reveal some energetic separation of the former three orbitals, arising from dative π-bonding formation. The planar structure of Ni(tmpz·NCO)$_2$ is confirmed by its diamagnetism; the very low μ_{eff} value is very likely caused by the temperature independent paramagnetic contribution to the total susceptibility.[23]

The most important results are the ascertainment of a nucleophilic addition in the Ni(II)-NCO^--tmpz and Co(II) - NCO^- - pz systems, and the isolation of coligand isomers, *viz* polymeric octahedral $Ni(NCO)_2(tmpz)_2$ and planar $Ni(tmpz\cdot NCO)_2$. Nucleophilic addition of this type and coligand isomerism were previously observed in analogous systems of Cu(II).[1] The present results are the first cases of these phenomena in the chemistry of other transition metals.

Both octahedral pz complexes are isostructural and their i.r. spectra are identical. The Ni(II) atom forms with the sterically hindered dmpz and tmpz ligands polymeric octahedral, cyanate N-bridged complexes with two heterocyclic molecules outside the coordination sphere, while Co(II) gives monomeric tetrahedral complexes. The latter fact also indicates that a nucleophilic addition occurs in $M(NCO)_2L_2$ complexes only if they are not tetrahedral structures.

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