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Cobalt(II) and Nickel(II) Complexes with the Polydentate Ligand Tris(3,5-dimethyl-1-pyrazolylethyl)amine, MeTPyEA. X-ray Investigation of two $[NiBr(MeTPyEA)]^+$ Cations: a Case of Distortional Isomerism

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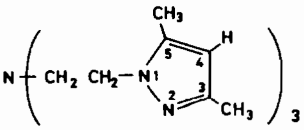
Nickel(II) and cobalt(II) complexes with the tetradentate ligand tris-(3,5-dimethyl-1-pyrazolylethyl)amine, MeTPyEA, have been prepared and characterized with the usual physicochemical methods. A case of distortional isomerism for the five-coordinate complex cation $[NiBr(MeTPyEA)]^+$ *has been ascertained through X-ray analyses of the two compounds* $[NiBr(MeTPyEA)]BPh_4 \cdot C_2H_5OH$ *and* $[NiBr(MeTPyEA)]BPh_4 \cdot (CH_3)_2CO$. *The two isomers have geometries approaching the ideal trigonal bipyramid and square pyramid, respectively. The structural rearrangements of the ligand framework occurring in these nickel complexes and in the four-coordinate* $[Co(MeTPyEA)](BPh_4)_2$ *complex are compared. Suggestions are proposed about the electronic factors which may determine the different coordination numbers, four, five, and six, within the series of 3d metal complexes with the ligand MeTPyEA.*

Introduction

In the past years we have investigated the coordinating behaviour toward 3d transition metal ions of polydentate ligands containing pyrazole rings as donor groups [1]. Ligands of this type have received general attention because conclusions concerning their metal complexes may have implications in the study of the active site structures of metallo-enzymes and metallo-proteins [2].

The recently synthesized ligand tris(3,5-dimethyl-1-pyrazolylethyl)amine, I, MeTPyEA, is of general interest. This is a tripod-like ligand containing one apical amine nitrogen atom and long chains which allow a large degree of flexibility to each arm. At the same time the methyl groups substituted in positions 3 and 5 of each ring strongly limit the coordinative possibilities on account of their steric hindrance.



(I)

As a preliminary account we reported the structure of the $[Co(MeTPyEA)](BPh_4)_2$ compound, which can be described as a trigonal pyramid distorted toward tetrahedron [3a]. The features of the electronic spectra of the same complex have also been reported elsewhere [3b].

We are now presenting a detailed report on the series of complexes formed by the MeTPyEA ligand in the presence of bi-positive metals of the first transition row. The study also includes the structural determination of the two $[NiBr(MeTPyEA)]BPh_4 \cdot C_2H_5OH$, *1*, and $[NiBr(MeTPyEA)]BPh_4 \cdot (CH_3)_2CO$, *2*, conformers.

Experimental

Synthesis of the Ligand

The ligand has been prepared as follows: 0.10 mol of $N(CH_2CH_2Cl)_3$ prepared as already described [4] and potassium 3,5-dimethylpyrazolate in slight excess to the stoichiometric ratio were allowed to reflux together in 600 cm^3 of anhydrous tetrahydrofuran for *ca.* 4 hours. The mixture was cooled to room temperature, the KCl eliminated by filtration, and the solution evaporated on a steam bath until a crude oil was obtained. The unreacted 3,5-dimethylpyrazole was eliminated by repeated crystallization from petroleum ether until the infrared spectrum of the recovered oil did not show the N–H stretching frequency of the 3,5-dimethylpyrazole. The final dense oil was used for the preparation of the complexes. Attempts to purify the crude oil by distillation at reduced pressure led to the decomposition of the compound.

Synthesis of the Cobalt(II) and Nickel(II) Complexes

Halo-, perchlorato-, and thiocyanato complexes were prepared by mixing warm solutions in ethanol or n-butanol (30 cm^3) of the appropriate metal salt (1.0 mmol) and the stoichiometric amount of the ligand. The solutions were concentrated by boiling to a small volume until crystals were obtained. In

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some cases cyclohexane or diethyl ether was added to promote crystallization. The tetraphenylborate and tetrafluoroborate complexes were prepared by adding concentrated solutions of $NaBPh_4$ in acetone and $NaBF_4$ in methanol, in excess to the stoichiometric amount, to warm solutions of the reactants in ethanol or n-butanol. In some cases the warm solutions were cooled to room temperature to effect crystallization. The [Co(NCS)(MeTPyEA)] BPh_4 complex was prepared as above by using $NaBPh_4$ in slight deficiency with respect to the stoichiometric ratio to prevent the formation of [Co(MeTPyEA)]$(BPh_4)_2$. The cobalt–zinc mixed complex has been prepared in ethanol with the usual method starting from solutions of $ZnBr_2$, $CoBr_2$, and the ligand in the stoichiometric ratio. Recrystallization from a mixutre of acetone and ethanol, ethanol and diethyl ether, n-butanol and cyclohexane was carried out depending on the various complexes.

By slow evaporation at room temperature of an acetone-ethanol solution of the [NiBr(MeTPyEA)]-BPh_4 derivative, a crop of yellow [NiBr(MeTPyEA)]-$BPh_4 \cdot C_2H_5OH$ and emerald [NiBr(MeTPyEA)] $BPh_4 \cdot CH_3COCH_3$ crystals was separated. The two compounds could be easily selected manually. The yellow complex heated at 160–165 °C transforms into a green isomer which melts at 217–219 °C. The same transformation occurs by grinding the yellow complex at room temperature. The emerald [NiBr(MeTPyEA)] $BPh_4 \cdot (CH_3)_2CO$ derivative melts at 223–224 °C. Analytical data are reported in Table I.

Physical Measurements

The apparatus and experimental techniques used for the magnetic measurements, electronic and infrared spectra, conductivity measurements and X-ray powder photographs are described in previous papers [1b, 5]. OH stretch. freq. for [NiX(MeTPyEA)] $BPh_4 \cdot C_2H_5OH$ (X = Cl, Br) at 3500 cm^{-1}; CO stretch. freq. for the [NiBr(MeTPyEA)] $BPh_4 \cdot (CH_3)_2CO$ at 1710 cm^{-1}; OH stretch. and HOH bending frequencies for the [Ni(H_2O)(MeTPyEA)] Y_2 (Y = ClO_4, BF_4: 3500 cm^{-1} and 1655 respectively, Y = BF_4; 3380, 1640 cm^{-1}, Y = ClO_4. CN stretch. freq. at 2080 for [Co(NCS)(MeTPyEA)] BPh_4 and 2045, 2080 cm^{-1} for [Co(NCS)(MeTPyEA)]$_2$ [Co(NCS)$_4$].

Crystal Data and Data Collection

The crystallographic work including crystal lattice determinations as well as the collections of the intensity data was carried out on a Philips PW 1100 automated diffractometer for both compounds by using monochromatized Mo-Kα radiation. The determination of crystal lattice parameters was carried out by using the standard routines [6].

The unit cell parameters of the *yellow* compound, *1*, are: $a = 23.018(5)$, $b = 16.085(5)$, $c = 12.178(4)$ Å, $\beta = 95.13(8)°$. The lattice is monoclinic space group $P2_{1/n}$. The calculated density for four unit formulae $C_{47}H_{59}N_7OBNiBr$ in the cell is 1.31 gcm^{-3}. A total of 2202 reflections with $\theta \leqslant 21.5°$ and with $I \geqslant 3\sigma(I)$ were considered observed and used throughout the structure solution and refinement. The data collection technique was ω–2θ. There was no hint of decay from the examination of three monitoring standard reflections. The crystal had a prismatic shape with dimensions 0.28 × 0.14 × 0.09 mm, and its faces were indexed in order to perform an absorption correction. The transmission factors varied between 0.95 and 0.86 by using a linear absorption coefficient of 13.2 for Mo-Kα.

TABLE I. Analytical Data for the Complexes.

	Found %			Calcd %		
	C	H	N	C	H	N
[Co(NCS)(MeTPyEA)] BPh_4 [a]	67.2	6.94	13.9	67.40	6.51	13.68
[Co(NCS)(MeTPyEA)]$_2$ [Co(NCS)$_4$] [b]	44.7	5.67	21.5	44.61	5.15	21.68
[Co(MeTPyEA)] $(ClO_4)_2$	39.4	5.54	15.5	39.33	5.19	15.29
[Co(MeTPyEA)] $(BF_4)_2$ [c]	41.0	5.63	15.7	40.94	5.40	15.91
[Co(MeTPyEA)] $(BPh_4)_2$ [d]	76.7	7.05	9.15	76.60	6.80	9.06
[Co(MeTPyEA)] [$CoBr_4$]	30.6	4.07	12.2	30.72	4.05	11.94
[Co(MeTPyEA)] [CoI_4]	25.1	3.33	9.56	25.00	3.30	9.72
[Co(MeTPyEA)] [$ZnBr_4$]	30.4	3.92	12.2	30.48	4.02	11.85
[NiCl(MeTPyEA)] $BPh_4 \cdot C_2H_5OH$ [e]	66.8	7.36	11.5	66.96	7.05	11.63
[NiBr(MeTPyEA)] $BPh_4 \cdot C_2H_5OH$	63.9	6.80	11.0	63.61	6.70	11.05
[NiBr(MeTPyEA)] $BPh_4 \cdot (CH_3)_2CO$	64.0	6.91	11.0	64.10	6.61	10.90
[Ni(NCS)(MeTPyEA)] BPh_4	67.5	6.85	13.6	67.42	6.52	13.67
[Ni(H_2O)(MeTPyEA)] $(ClO_4)_2$	38.5	5.35	14.8	38.26	5.35	14.87
[Ni(H_2O)(MeTPyEA)] $(BF_4)_2$	39.5	5.76	15.3	39.79	5.57	15.47

[a] Co: found 7.05, calcd 7.19. [b] S: found 14.8, calcd 14.89. [c] Co: found 9.22, calcd 9.57. [d] Co: found 5.34, calcd 5.45. [e] Ni: found 6.58, calcd 6.96.

The unit cell parameters of the *emerald* compound, *2*, are: $a = 38.809(9)$, $b = 13.134(6)$, $c = 20.442(6)$ Å, $\beta = 109.67(11)^\circ$, monoclinic, space group $C_{2/c}$. The calculated density for eight unit formulae $C_{48}H_{59}N_7OBNiBr$ in the cell is 1.21 gcm^{-3}. 1487 reflections collected up to $\theta \leqslant 20^\circ$ had $I \geqslant 3\sigma(I)$ and were considered observed. The crystal was prismatic in shape with dimensions 0.12 × 0.08 × 0.03 mm along the principal axes. In view of its smallness no absorption correction was applied. The crystall appeared opaque under the microscope with crackings on its surfaces, thus revealing a poor crystalline quality. On the other hand no such aspect is observable when the crystal is still merged in the mother solution, suggesting that a good crystallinity in this species is to be associated with saturation with acetone molecules.

Structure Determinations

All the crystallographic computing was performed on a SEL 32/70 computer by using a selection of programs from SHELX 76 [7] and XRAY76 [8] systems, and other locally written programs. The drawings were made by using the program PLUTO [9].

A combined use of direct methods and Patterson routines were used for the solution of both structures. Subsequent F_o and ΔF maps allowed the localization of all the non-hydrogen atoms, including peaks which were attributed to the solvent atoms.

Refinement was undertaken by means of full matrix least squares techniques; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is taken as $1/\sigma^2(F_o)$.

The following strategy was adopted for the refinement of both structures. Initial cycles, allotting only isotropic temperature factors to all the non-hydrogen atoms, were followed by final cycles where the Ni, Br and N atoms were refined by using the anisotropic model of the thermal motion.

Rigid bodies constraints (D_{6h}) were applied to all the phenyl groups of the tetraphenylborate anions. Hydrogen atoms were introduced at calculated positions ($d_{C-H} = 0.95$ Å). Final R factors are 0.069 and 0.101 for the *yellow* and *emerald* compounds respectively.

A separate comment must be made about the treatment of the disordered solvent molecules in each structure. Five major peaks were initially found in ΔF maps of structure *1*. All the peaks were treated as carbon atoms in the subsequent refinement although the chemical information indicated the presence of an alcohol molecule. The peak labelled as C(46) was predominant over the others, and was assigned a population parameter of 1. The two couples of remaining peaks were considered as the split images of two atoms, and the sum of their p.p. was constrained to 1. The final values of the p.p. of C(48) and C(50) are about 0.7.

The elemental analysis is consistent with the presence of one acetone molecule in the *emerald* compound, *2*. We have already mentioned the critical influence of the solvent on the crystallinity of the compound. Due to the great disorder affecting the solvent, it was not possible to build a suitable model for an acetone molecule. Four peaks were isolated and refined as carbon atoms. The difficulties encountered in the refinement of the solvent as well as the limited number of observed reflections for this structure account for the poor convergence of the refinement. This is clearly evident in the high standard deviations both on the atomic parameters and on the derived bond distances and angles. However, we believe that the chemical information contained in this structure is correct and suitable for the subsequent discussion.

Final values of the atomic parameters are reported in Tables II and III. Tables of structure factors are available from the Editor on request.

Results and Discussion

Nickel Complexes

Complexes with the formulae [NiX(MeTPyEA)]-BPh_4·solv (X = Cl, solv = ethanol; X = Br, solv = ethanol, acetone) (a), [Ni(NCS)(MeTPyEA)]BPh_4 (b), and [Ni(H_2O)(MeTPyEA)]Y_2 (Y = ClO_4, BF_4) (c), have been prepared. The coordinating capability of the anion in the reactant nickel(II) salt determines the formation of either type a, b or c complexes. The magnetic moment values are indicative of two unpaired electrons in all of the complexes and are temperature independent in the range 298–80 K (Table IV). The molar conductivities are in the range expected for 1:1 (a and b complexes) and 1:2 electrolytes (c complexes) (Table IV) [10]. This information, together with the reflectance spectra of the solids and the absorption spectra in acetone, indicate that all of the complexes can be assigned the same five-coordinate geometry in the solid state and also in acetone solution [11]. The only possible exception is the *yellow* complex [NiBr(MeTPyEA)]BPh_4·C_2H_5OH, *1*, which has a solid state electronic spectrum slightly different from those of the other nickel complexes here reported but which is still indicative of five-coordination (Table IV and Fig. 1). However, in acetone solution, the complex *1* turns into an emerald color and the absorption spectrum is now similar to those of the other nickel complexes (Table IV). Moreover by heating at *ca.* 160 °C or by grinding the *yellow* compound, *1*, its yellow colour turns to green. This green isomer has a magnetic moment and electronic spectra, both in the solid state and in acetone solution, quite similar to those of the *emerald* [NiBr(MeTPyEA)]BPh_4·acetone, *2*, derivative (Fig. 1). The same type of five-coordinate geometry

TABLE II. Atomic Parameters for the NiBr(MeTPyEA)-$\mathrm{BPh_4 \cdot CH_3CH_2OH}$ Complex.[a]

Atom	X	Y	Z	U(A^2)
Ni	4623(1)	1429(1)	1844(2)	39(1)
Br	4436(1)	−64(1)	1818(3)	86(1)
N1	5201(4)	2316(6)	1211(13)	47(6)
N2	4078(4)	1521(7)	331(14)	51(7)
N3	4309(4)	1551(7)	−624(12)	46(7)
N4	5307(4)	1196(7)	3123(13)	44(6)
N5	5834(4)	1003(7)	2689(15)	49(7)
N6	4170(4)	2202(6)	2763(12)	45(7)
N7	4289(4)	3029(7)	2868(12)	46(7)
C1	5005(6)	2584(9)	78(15)	50(4)
C2	4896(5)	1876(9)	−716(16)	57(4)
C3	5818(5)	1977(8)	1209(15)	50(4)
C4	5900(6)	1102(9)	1592(15)	52(4)
C5	5228(5)	3048(8)	1971(14)	48(4)
C6	4639(5)	3445(8)	2114(14)	52(4)
C7	3104(7)	1171(10)	923(17)	69(5)
C8	3529(7)	1274(9)	86(17)	56(5)
C9	3422(7)	1148(9)	−1024(18)	60(5)
C10	3935(6)	1303(8)	−1492(18)	51(4)
C11	4086(7)	1279(9)	−2617(16)	65(5)
C12	4932(7)	1250(11)	4967(17)	76(6)
C13	5388(7)	1110(10)	4196(18)	56(5)
C14	5978(6)	863(8)	4472(18)	55(4)
C15	6238(6)	819(9)	3569(16)	48(4)
C16	6855(6)	623(10)	3398(18)	69(5)
C17	3525(7)	1202(9)	3741(18)	69(5)
C18	3768(6)	2045(9)	3503(15)	51(4)
C19	3647(6)	2771(8)	4025(16)	56(4)
C20	3974(7)	3392(10)	3599(18)	67(5)
C21	4020(7)	4308(10)	3872(19)	82(6)
B1	3624(6)	4614(9)	−2395(18)	40(4)
C22	3657(4)	5496(5)	−3104(9)	48(4)
C23	4097(4)	5601(5)	−3809(9)	63(5)
C24	4101(4)	6305(5)	−4478(9)	87(6)
C25	3665(4)	6903(5)	−4442(9)	86(6)
C26	3224(4)	6798(5)	−3738(9)	71(5)
C27	3221(4)	6094(5)	−3069(9)	57(4)
C28	4316(13)	4202(6)	−2280(7)	43(4)
C29	4497(3)	3616(6)	−3023(7)	53(4)
C30	5084(3)	3393(6)	−2991(7)	66(5)
C31	5490(3)	3757(6)	−2217(7)	62(5)
C32	5309(3)	4343(6)	−1475(7)	65(5)
C33	4722(3)	4565(6)	−1506(7)	50(4)
C34	3157(4)	3978(5)	−3141(8)	48(4)
C35	3145(4)	3135(5)	−2874(8)	52(4)
C36	2740(4)	2609(5)	−3441(8)	67(5)
C37	2347(4)	2927(5)	−4276(8)	60(5)
C38	2359(4)	3770(5)	−4543(8)	61(4)
C39	2764(4)	4295(5)	−3975(8)	49(4)
C40	3433(4)	4718(5)	−1105(11)	44(4)
C41	3373(4)	4006(5)	−472(11)	79(5)
C42	3202(4)	4074(5)	595(11)	89(6)
C43	3090(4)	4855(5)	1028(11)	91(6)
C44	3150(4)	5568(5)	394(11)	85(6)
C45	3322(4)	5499(5)	−672(11)	68(5)
C46*	2032(14)	2613(21)	2415(32)	211(14)
C47*	1961(10)	3390(16)	2295(26)	116(9)
C48*	1390(37)	2980(53)	2510(107)	80(33)
C49*	1701(27)	3957(49)	2439(63)	301(41)
C50*	1306(12)	3163(17)	3283(33)	123(16)

(continued ↑)

TABLE II *(continued)*

[a] Coordinates multiplied by 10^4, temperature factors by 10^3. Anisotropic temperature factors for Ni, Br and N atoms are given as: U(eq.) = (U11 + U22 + U33)/3. Atoms labelled with * belong to the alcohol solvent molecule (see text).

TABLE III. Atomic Parameters for the NiBr(MeTPyEA)-$\mathrm{BPh_4 \cdot (CH_3)_2CO}$ Complex.[a]

Atom	X	Y	Z	U(A^2)
Ni	3970(1)	4786(4)	390(3)	30(3)
Br	4125(1)	5449(4)	−618(3)	78(4)
N1	3610(8)	3609(21)	−45(15)	39(21)
N2	3928(8)	4618(21)	1305(15)	57(21)
N3	3583(8)	4376(20)	1421(16)	49(23)
N4	3556(9)	5745(26)	145(19)	47(27)
N5	3271(9)	5694(24)	−504(18)	44(23)
N6	4469(9)	2885(30)	665(16)	63(30)
N7	4460(8)	3999(28)	684(16)	48(27)
C1	3844(9)	2730(26)	−117(18)	42(11)
C2	4130(9)	2337(27)	529(17)	38(12)
C3	3382(10)	3910(26)	−756(19)	43(12)
C4	3098(8)	4731(27)	−795(17)	38(10)
C5	3390(9)	3274(26)	356(18)	38(11)
C6	3292(9)	4071(26)	813(19)	39(11)
C7	4902(11)	5376(34)	834(21)	77(14)
C8	4809(13)	4256(35)	835(21)	54(14)
C9	5030(11)	3414(32)	956(20)	54(13)
C10	4830(12)	2568(35)	844(20)	48(12)
C11	4913(12)	1520(38)	879(23)	87(17)
C12	3902(11)	7147(32)	921(23)	76(15)
C13	3590(12)	6792(41)	279(24)	65(14)
C14	3315(12)	7402(35)	−201(25)	82(15)
C15	3128(12)	6640(38)	−682(23)	57(14)
C16	2773(13)	6820(37)	−1359(25)	102(17)
C17	4532(11)	5150(33)	2155(22)	90(16)
C18	4107(11)	4878(32)	1973(25)	61(13)
C19	3939(9)	4707(30)	2485(19)	51(12)
C20	3590(9)	4407(24)	2072(20)	20(10)
C21	3244(10)	4193(27)	2274(19)	49(12)
B	1781(11)	4837(33)	−1340(21)	38(13)
C22	2093(6)	4056(18)	−1479(10)	26(11)
C23	2218(6)	3253(18)	−1011(10)	35(11)
C24	2457(6)	2531(18)	−1119(10)	31(10)
C25	2571(6)	2612(18)	−1695(10)	30(10)
C26	2447(6)	3414(18)	−2162(10)	51(12)
C27	2208(6)	4136(18)	−2054(10)	46(12)
C28	1919(5)	4976(18)	−460(13)	54(13)
C29	1696(5)	4690(18)	−80(13)	40(11)
C30	1823(5)	4790(18)	642(13)	83(15)
C31	2172(5)	5176(18)	983(13)	51(12)
C32	2395(5)	5463(18)	603(13)	47(12)
C33	2268(5)	5363(18)	−119(13)	53(12)

(continued on facing page)

TABLE III *(continued)*

Atom	X	Y	Z	U(A^2)
C34	1363(8)	4339(16)	−1648(12)	40(12)
C35	1069(8)	4933(16)	−1627(12)	91(16)
C36	712(8)	4574(16)	−1926(12)	80(14)
C37	649(8)	3620(16)	−2246(12)	59(13)
C38	943(8)	3027(16)	−2266(12)	82(15)
C39	1300(8)	3386(16)	−1967(12)	61(13)
C40	1746(8)	5921(16)	−1750(12)	40(12)
C41	1840(6)	6847(21)	−1402(10)	42(12)
C42	1784(6)	7756(21)	−1776(10)	63(13)
C43	1634(6)	7738(21)	−2500(10)	67(14)
C44	1539(6)	6812(21)	−2848(10)	72(15)
C45	1595(6)	5903(21)	−2474(10)	60(14)
C46*	621(12)	4566(34)	421(22)	84(15)
C47*	1009(13)	4598(36)	596(24)	101(16)
C48*	779(15)	5303(45)	−519(29)	164(23)
C49*	846(18)	5682(50)	385(41)	180(24)

[a]Coordinates multiplied by 10^4, temperature factors by 10^3. Anis. temp. factors are given as U(eq.) for Ni, Br and N atoms. Atoms labelled with * belong to the acetone solvent molecule (assigned population parameter = 0.5).

can be consequently assumed for both these complexes. Whether the geometry is square pyramidal (SqP) or trigonal bipyramidal (TBP) is hardly predictable on the basis of spectral criteria alone. At most, the spectra indicate that the complexes are somewhat distorted from both the two limiting geometries [11].

We have therefore carried out the X-ray study of both the *yellow* [NiBr(MeTPyEA)]$BPh_4 \cdot C_2H_5OH$, *1*, and the *emerald* [NiBr(MeTPyEA)]$BPh_4 \cdot (CH_3)_2CO$, *2*, compounds. This analysis should reveal the structural arrangement which takes place in the transformation of the yellow into the green isomer. Moreover these structures and that of the [Co(MeTPyEA)]$(BPh_4)_2$ complex already at hand [3a] should provide informative hints about the coordination geometry in the other complex cations of the series [MX(MeTPyEA)]$^+$ (M = Cr, Mn, Fe, Co). Some preliminary accounts of a few of the above complexes have been reported elsewhere [12].

Both the *yellow*, *1* and the *emerald*, *2* isomers are comprised of complex cations of formula [NiBr(MeTPyEA)]$^+$, BPh_4^- anions, and interspersed solvent molecules.

TABLE IV. Some Physical Data for the Complexes.

	μ_{eff}, μ_B[a] (298 K)	Λ_M[c] S cm^2 mol^{-1}	State[d]	Electronic spectra, μm^{-1} (ϵ_{molar} for soln in parentheses).
[Co(NCS)(MeTPyEA)]BPh_4	4.43		R	0.57, 1.29, 1.62, 195
		92	A	0.56(48), 1.27(42), 1.65(249), 1.92(170)
[Co(NCS)(MeTPyEA)]$_2$[(Co(NCS)$_4$]	4.51[b]		R	0.76, 1.28, 1.64, 1.96
		135	A	0.78(318), 1.26(183), 1.64(2360), 1.96(396)
[Co(MeTPyEA)]$(ClO_4)_2$	4.20		R	0.73, 1.27, 1.71, 2.16
		180	A	0.72(49), 1.23(98), 1.67(740), 1.72(680), 2.06(94)
[Co(MeTPyEA)]$(BF_4)_2$	4.14		R	0.71, 1.26, 1.73 2.15
		198	A	0.73(44), 1.22(90), 1.67(640), 1.72(570), 2.06(92)
[Co(MeTPyEA)]$(BPh_4)_2$	4.22		R	0.71, 1.26, 1.72, 2.15
		165	A	0.72(54), 1.23(100), 1.66(645), 1.73(570), 2.06(87)
[Co(MeTPyEA)] [$CoBr_4$]	4.48[b]		R	0.56, 0.70, 1.21, 1.44, 1.73, 2.06
		248	M	0.71(41), 1.24(73), 1.67(325), 1.72(300), 2.06(55)
[Co(MeTPyEA)] [CoI_4]	4.54[b]		R	<0.50, 0.70, 1.11, 1.30, 1.72, 2.06
		263	M	0.72(40), 1.24(77), 1.67(530), 1.73(414), 2.08(83)
[Co(MeTPyEA)] [$ZnBr_4$]	4.26		R	0.72, 1.22, 1.73, 2.04
		422	W	1.33(9), 1.66(46), 1.72(42), 2.04(12)
[NiCl(MeTPyEA)]$BPh_4 \cdot C_2H_5OH$	3.27		R	0.63, 0.80, 1.21, 1.61, 2.56
		88	A	0.61(30), 0.78(28), 1.16(15), 1.23(15), 1.61(41), 2.56(181)
[NiBr(MeTPyEA)]$BPh_4 \cdot C_2H_5OH$	3.24		R	0.68, 1.39, 2.00, 2.35
		91	A	0.63(30), 0.80(32), 1.14(20), 1.23(21), 1.61(40), 2.50sh
[NiBr(MeTPyEA)]$BPh_4 \cdot (CH_3)_2CO$	3.26		R	0.64, 0.81, 1.25, 1.62, 2.59
		92	A	0.61(31), 0.79(29), 1.15(17), 1.22(20), 1.61(54), 2.56(320)
[Ni(NCS)(MeTPyEA)]BPh_4	3.21		R	0.65, 0.78, 1.18, 1.27, 1.74, >2.70
		91	A	0.66(62), 0.76sh, 1.18(20), 1.28(19), 1.71(45), >2.70
[Ni(H_2O)(MeTPyEA)]$(ClO_4)_2$	3.18		R	0.68, 0.84, 1.24, 1.68, 2.60
		181	A	0.68(30), 0.82(42), 1.19(20), 1.28(18), 1.67(32), 2.66(140)
[Ni(H_2O)(MeTPyEA)]$(BF_4)_2$	3.22		R	0.68, 0.85, 1.24, 1.70, 2.67
		184	A	0.68(30), 0.82(41), 1.19(20), 1.28(18), 1.67(30), 2.66(130)

[a] $1\mu_B = 9.27 \times 10^{-24}$ Am^2. [b]Average value per metal atom. [c]For *ca.* 10^{-3} mol dm^{-3} solutions in the same solvent as electronic spectra; S = kg^{-1} m^{-2} s^3 A^2 = Ω^{-1}. [d]R, diffuse reflectance; A, acetone, M, methanol, W, water solutions.

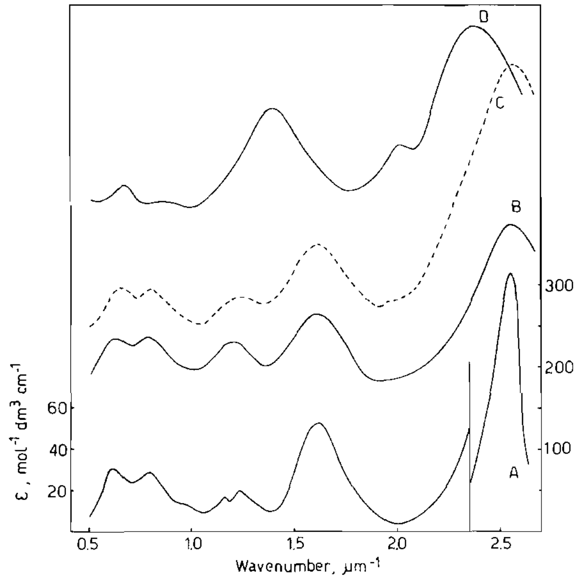


Fig. 1. Electronic spectra of [NiBr(MeTPyEA)]BPh$_4$·(CH$_3$)$_2$CO: absorption spectrum in acetone, A; diffuse reflectance spectrum, B. Diffuse reflectance spectra of [NiBr(MeTPyEA)]BPh$_4$·C$_2$H$_5$OH: green isomer, C; yellow isomer, D.

Figure 2 shows sketch drawings of the inner coordination spheres of the two isomeric cations. The ideal geometries of five-coordination, namely TBP and SqP, are approached in compounds *1* and *2* respectively. In the former compound two pyrazole nitrogen donor atoms [N(2), N(4)] of the MeTPyEA ligand occupies the two axial positions of TBP, whereas the central amine [N(1)] and the third pyrazole nitrogen donor atom [N(6)] are lying in the equatorial plane together with the nickel and bromine atoms.

The square pyramid of the *emerald* compound *2* is formed at the equatorial positions by the three pyrazole nitrogen donor atoms of MeTPyEA and by a bromine atom. The apical position is occupied by the central amine nitrogen atom [N(1)]. From the examination of Table V, which reports a selection of bond distances and angles in the two structures, we observe only minor differences in terms of bond angles between the inner coordinations of the two NiN$_4$ fragments. Thus we have two trans pyrazole rings forming angles, N(2)–Ni–N(4), of 166.6(5)° and 170.3(1.4)° in *1* and *2*, respectively, while all the other N–Ni–N angles vary in the narrow range 86.4–100.0° in the two compounds. Conversely, the relative position of the bromine atom changes significantly in going from *1* to *2*. These atoms lie in the plane formed by Ni, N(1) and N(6) atoms in both cases, but the equatorial Br–Ni–N(6) angle increases from 120.9(3)° in *1* to 163.3(9)° in *2*. Disregarding for the moment the observed significant differences in the metal–ligand bond lengths, the difference between the *yellow* and the *emerald* NiN$_4$Br chromophores could be thought, in a first approximation, as being simply due to a migration of the bromine atom in the equatorial plane. The opening of an equatorial angle of TBP to form SqP through a pathway maintaining a C_{2v} symmetry (intermediate between D_{3h} and C_{4v}), is known as Berry pseudorotation [13]. However the matter is not so simple in the present case. Major conformational rearrangements take place also within the ligand framework. Figure 3 shows views of the complex cations down the direction of the lone pair at the apical amine nitrogen atom. By keeping the same orientation for the two C$_1$, C$_3$, C$_5$ groupings, the different spatial conformations of the three arms of the ligand can be readily estimated. In particular the two pictures clearly show the different torsions of the pyrazole

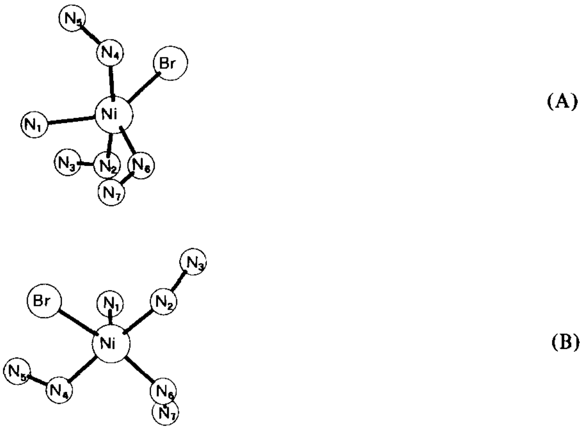


Fig. 2. Sketch drawings of the inner coordination sphere of the complex cations [NiBr(MeTPyEA)]$^+$: yellow isomer *1*, A; emerald isomer *2*, B.

TABLE V. Selected Bond Distances (Å) and Angles (°) in the [NiBr(MeTPyEA)]$^+$ Complex Cations.

	Yellow *1*	Emerald *2*
Ni–Br	2.439(2)	2.489(8)
Ni–N(1)	2.141(11)	2.072(27)
Ni–N(2)	2.138(14)	2.067(32)
Ni–N(4)	2.146(12)	1.969(32)
Ni–N(6)	2.023(12)	1.942(33)
Br–Ni–N(1)	140.0(4)	102.08(9)
Br–Ni–N(2)	88.2(3)	87.8(1.2)
Br–Ni–N(4)	87.4(3)	88.2(1.2)
Br–Ni–N(6)	120.9(3)	163.3(9)
N(1)–Ni–N(2)	88.8(5)	100.0(1.2)
N(1)–Ni–N(4)	86.4(5)	89.6(1.2)
N(1)–Ni–N(6)	99.0(5)	93.8(1.2)
N(2)–Ni–N(4)	166.6(5)	170.3(1.4)
N(2)–Ni–N(6)	98.2(5)	91.7(1.3)
N(4)–Ni–N(6)	94.9(5)	89.6(1.3)

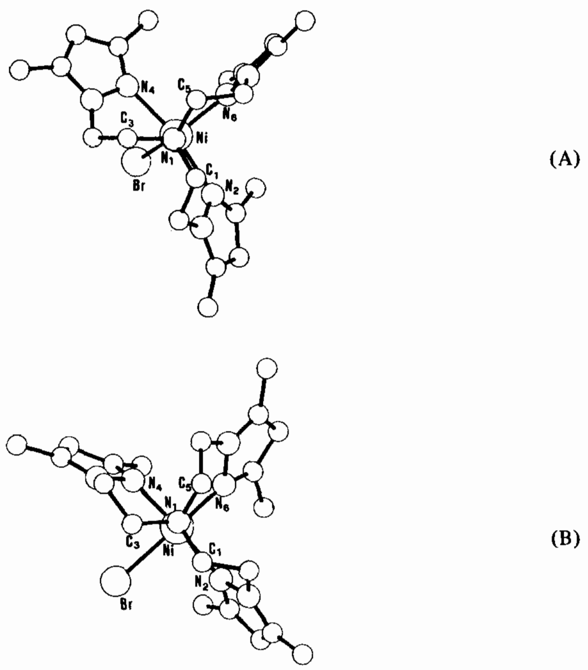
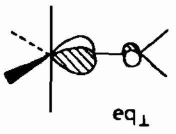


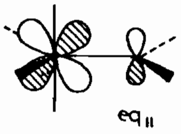
Fig. 3. Sketch drawings of the complex cations $[NiBr(Me\text{-}TPyEA)]^+$: yellow isomer *1*, A; emerald isomer *2*, B.

rings with respect to the coordinative Ni–N bonds. For example, the plane of the ring containing N(6) in *1* is practically lying in the equatorial plane of TBP, while it forms a dihedral angle of *ca.* 38° with the SqP apical direction Ni–N(1) in *2*. The ring containing N(4) has the same orientation with respect to the latter direction but the third ring is almost parallel to this direction.

As shown by Rossi and Hoffmann [14] the relative orientation of single faced π donor ligands, such as pyrazole, may play an important role in determining the relative stability of ML_5 complexes in which they enter as substituent. To summarize their results, no effective discrimination between possible orientations is expected when these substituents are in axial positions of TBP. For an equatorial π donor ligand, there are two extreme possibilities of interaction, shown as $eq_\perp$ and $eq_\parallel$ in *a* and *b*, respectively. If both the metal orbitals are filled the site of least interaction is preferred. On the basis of minimum overlap arguments this site corresponds to the $eq_\parallel$ conformation.



a

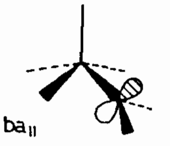


b

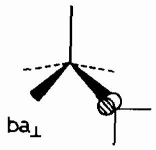
In fact the metal d orbital in *a* is hybridized while in *b* it is not. The conformation of the equatorial pyrazole in *1* is just $eq_\parallel$.

This kind of analysis becomes more complicated for SqP ML_5 complexes and the conclusions are strongly dependent on the degree of pyramidalization of SqP.

For single faced π donor ligands in basal positions the conformation $ba_\parallel$, *c*, is more destabilized than the conformation $ba_\perp$, *d*. Actually the former conformation is never observed in compound *2* while the latter is found for one pyrazole ring, the one containing N(2). The other two rings have conformations intermediate between $ba_\parallel$ and $ba_\perp$, allegedly less destabilizing.



c



d

Extreme caution however is required in applying the arguments of Rossi and Hoffmann to our compounds. Their models in fact have high symmetries while ours have none; this discussion based in terms of four electron destabilizing interactions, holds for d^8 low-spin species. It is not directly applicable to d^8 high-spin species. The steric effects associated with the ligand overall conformation may easily override the electronic effects.

Some trends observed for the Ni–N distances may be rationalized by looking at the relative orientations of the pyrazole rings. Thus, the two long apical distances (2.138(14) and 2.146(12) Å) in compound *1*, are expected to be equal on account of the lack of electronic discrimination between the orientations of the rings in the apical positions.

In compound *2*, the Ni–N(pyrazole) distances are all basal in SqP. Two of them are short (1.97(3) and 1.94(3)) while the Ni–N(2) distance is distinctly longer (2.07(3)). Perhaps significantly, the orientation of the relative pyrazole is unique in being of $ba_\perp$ type and corresponds to the destabilizing orbital interaction, shown in *d*.

In conclusion, we point out that the present structures represent an interesting case of distortional isomerism. Examples of distortion isomers in five-coordinated geometries are not uncommon for copper(II) complexes [15] and the individual structures have been used to map the change from one stereochemistry to another. At least one example of distortional isomerism is also known for the low-spin cobalt(II) ion in the $[Co(dpe)_2Cl]^+$ complex cation [16] (dpe is 1,2-diphenylphosphinoethane) and for the low-spin d^8 species $[Ni(CN)_5]^{3-}$ [17].

Cobalt Complexes

The cobalt(II) complexes have formulae [Co(MeTPyEA)]Y_2 (Y = BF_4, ClO_4, BPh_4) (a), [Co(MeTPyEA)][MX_4] (M = Co, X = Br, I; M = Zn, X = Br) (b), [Co(NCS)(MeTPyEA)]BPh_4 (c), and [Co(NCS)(MeTPyEA)]$_2$[Co(NCS)$_4$] (d). The magnetic moment values are consistent with three unpaired electrons for each cobalt atom (Table IV). The values of molar conductivities in acetone solutions of complexes a and c are in the range usually found for 1:2 and 1:1 electrolytes respectively (Table IV). The high values of conductivity of the complexes b in CH_3OH solutions suggest an extensive solvolysis of the MX_4^{2-} counterion. The electronic spectra of complexes a and of [Co(MeTPyEA)][$ZnBr_4$] are quite similar to each other (Fig. 4); the reflectance spectra of the compounds of b type which contain two cobalt atoms have two additional bands at *ca.* 0.5 and 1.3–1.4 μm^{-1} due to the tetrahedral CoX_4^{2-} species. These intense bands disappear in the absorption spectra of the complexes in CH_3OH and H_2O solutions thus confirming that a solvolysis of the tetrahalogen species occurs in solution.

The electronic spectra of [Co(NCS)(MeTPyEA)]$^+$ cations, apart from the bands attributable to the tetrahedral [Co(NCS)$_4$]$^{2-}$ ion in complex d, are indicative of five-coordination (Fig. 4) [18].

It has been previously found by means of X-ray analysis that in the [Co(MeTPyEA)](BPh_4)$_2$ complex the cobalt(II) is tetracoordinated by the four nitrogen atoms of the ligand in an unique tetrahedrally distorted trigonal pyramidal structure [3a]. The same type of structure can be assigned to all of the [Co(MeTPyEA)]$^{2+}$ species here reported, on the basis of spectral and other physicochemical measurements.

The sole cobalt complex which can be considered fivecoordinate is the one obtainable in the presence of NCS^- anions. The latter ligand enters the cobalt coordination sphere probably on account of its low steric hindrance and its strong donor power. Parenthetically, the only vanadium(II) species which has been obtained with the ligand MeTPyEA is the octahedral complex [V(NCS)$_2$(MeTPyEA)], with as many as two NCS^- ions coordinated to the metal [12].

In the cobalt complexes, can the NCS^- group reside at the unoccupied axial position of the Co(MeTPyEA) fragment? The structure of the [Co(MeTPyEA)]$^{2+}$ cation showed that the methyl groups in position 5 of each pyrazole ring prevent any other approaching co-ligand from entering the coordination sphere along the axial direction. Moreover the ir spectra and the X-ray powder photograph patterns of the [Co(NCS)(MeTPyEA)]BPh_4 are distinctly different from those of [Co(MeTPyEA)](BPh_4)$_2$ but are essentially the same as those of [NiBr(MeTPyEA)]$\cdot BPh_4 \cdot (CH_3)_2CO$.

In conclusion, the coordination number five is prevalent in most cases when bivalent 3d metal ions are coordinated by the MeTPyEA ligand (Table VI). On the basis of analogies between electronic and ir spectra as well as X-ray powder photographs, we can assert that in no case is five-coordination achieved while the polydentate ligand keeps C_{3v} symmetry. Moreover it is only in the presence of d^3 and d^7 electron counting that coordinations other than five are preferred. More structures would be needed to make a clear cut picture of all the coordinating possibilities of the ligand. However the six-coordination of vanadium(II) confirms the findings already reported by us about the stability of the t_{2g}^3 configuration in the octahedral field and the spatial requirements of the large ionic radius of V^{2+} [1a]. In order to try to explain the preferred four-coordination of cobalt(II) with the MeTPyEA ligand, we have carried out some extended Hückel calculations on a simple [Co(NH_2)$_3NH_3$]$^-$ model with imposed C_{3v} symmetry [19]. The model approximates our real mole-

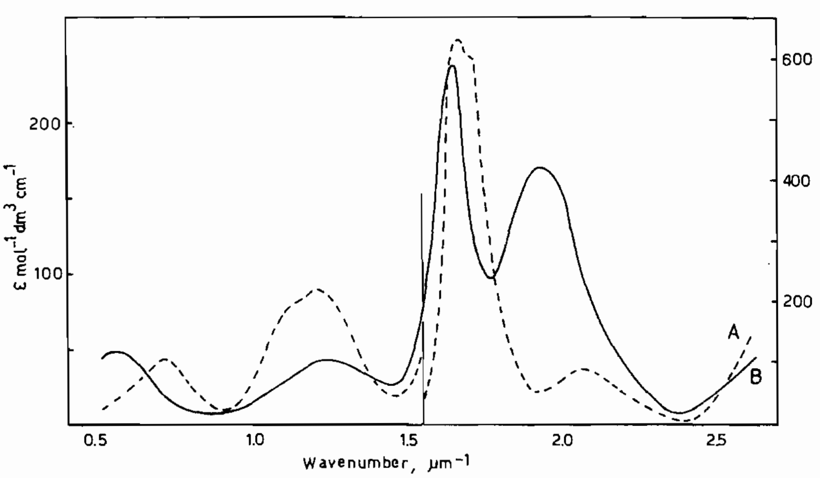


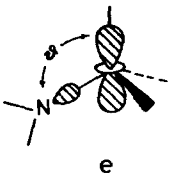
Fig. 4. Absorption spectra in acetone of [Co(MeTPyEA)](BPh_4)$_2$, A, and [Co(NCS)(MeTPyEA)]BPh_4, B.

TABLE VI. Summary of the Complexes with the Ligand MeTPyEA (L).

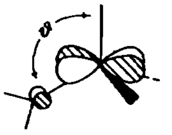
	$[V(NCS)_2(L)]$	$[CrX(L)]^{+}$ *	$[MnX(L)]^{+}$	$[FeX(L)]^{+}$ *	$[Co(L)]^{2+}$	$[Co(NCS)(L)]^{+}$	$[NiX(L)]^{n+}$ *
Coord. Number	6	5	5	5	4	5	5

*The yellow $[NiBr(L)]BPh_4 \cdot C_2H_5OH$ is strictly isomorphous with the other two complexes on the basis of ir evidence and X-ray powder photograph patterns.

cule, for it has an apical amine group and three equatorial single faced π donor NH_2^- groups. Each NH_2^- group was assigned the $eq_{\perp}$ orientation. The level ordering of the upper metal d orbitals is a function of the pyramidalization of the fragment as shown in Fig. 5. At $\theta = \theta_{tetr.}$, the z^2 orbital is calculated below the 2e level (xy, $x^2 - y^2$). Adjusting the geometry toward the trigonal pyramid, there is increasing σ antibonding between the basal donors and z^2, and also increasing π antibonding between the filled π orbitals of the NH_2^- ions and the metal xy and $x^2 - y^2$ orbitals. The situation is depicted in *e* and *f* for an equatorial ligand. The destabilization of a_1 grows faster than that of 2e but at $\theta = 100$ the experimental value in the cobalt structure, a_1 is still below 2e. The trend is somewhat different from that found for $C_{3v}M(CO)_4$ models where the 2e level stabilizes with increasing pyramidalization due to the π acceptor capabilities of the carbonyls [20]. The pyrazole rings which have some high-lying π acceptor molecular orbitals are allegedly intermediate between the two cases. Whether the a_1 level lies higher or lower than the 2e level is not of crucial importance for the stability of the d^7 trigonal pyramidal metal complex. In fact three unpaired electrons occupy the highest d orbitals and receive exchange energy stabilization in any case. On going to the d^8 configuration, Jahn–Teller instability is expected in the hypothetical $[Ni(MeTPyEA)]^{2+}$ cation, if the a_1 level lies above the 2e level [21]. Conversely, a reverse level ordering should not induce distortions as observed in several tetrahedral nickel(II) complexes [21]. In the latter case, however, a possible source of distortion derives from the full population of the σ antibonding a_1 level which stretches the Ni–N(ap.) bond in a manner perhaps not tolerable by the polydentate ligand. Whatever the origin of the distortion, the ligand rearranges about the metal thus creating an opening for an incoming co-ligand. Also a d^6 complex $[Fe(MeTPyEA)]^{2+}$ cannot be isolated. In this case the Jahn–Teller instability (readily seen for the degenerate 1e level) would be occupied by three electrons in a d^6 high spin configuration.



e



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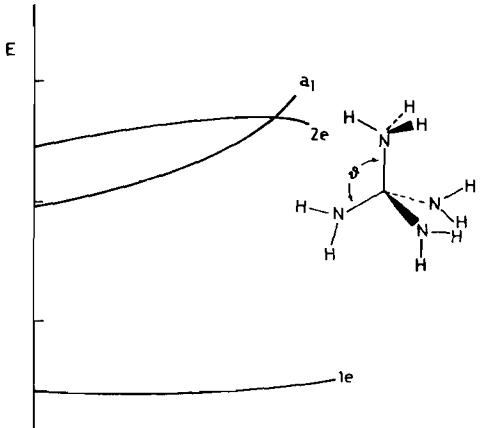

Fig. 5. Energy variation of the frontier orbitals in the $[Co(NH_2)_3NH_3]^-$ model as a function of the θ angle.

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